

STANDARDS DEVELOPMENT BRANCH OMOE



3 6936 00000 2422

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

THE SHERATON CENTRE
TORONTO, ONTARIO,
CANADA

Part B
Water Quality Research

TD
172.5
.057
1986
part B
MOE

TD
172.5
.057
1986
part B

Proceedings : technology
transfer conference

76021

ISSN 0-825-4591

PROCEEDINGS

TECHNOLOGY TRANSFER CONFERENCE

December 8 & 9, 1986

The Sheraton Centre

External Research Projects

**PART B
WATER QUALITY RESEARCH**

**Organized by
Research Advisory Committee**

Sponsored by

**Corporate Resources Division
Ministry of the Environment
Ontario
CANADA**

**HAZARDOUS CONTAMINANTS
COORDINATION BRANCH
135 ST. CLAIR AVENUE WEST
TORONTO, ONTARIO M5T 1A5**

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

Goal Statement

"To achieve and maintain a quality of the environment - including air, water and land - that will protect human health and the ecosystem and will contribute to the well-being of the people of Ontario."

ACKNOWLEDGEMENTS

The Conference Committee would like to thank the speakers and organizers for their valuable contributions.

DISCLAIMER

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

INTRODUCTION

The Ontario Ministry of the Environment holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario universities and by private research organizations.

The papers presented at the Technology Transfer Conference held in December 1986 are presented in Conference Proceedings. These Proceedings are divided into five parts corresponding to the conference sessions dealing with:

Part A: Air Quality Research ;
Part B: Water Quality Research;
Part C: Liquid & Solid Waste;
Part D: Analytical Methods; and
Part E: Environmental Economics.

This part is a collation of those papers presented at Session B of the Conference.

For further information on any of the projects, the reader is kindly referred to the Principal Investigators or to the Research Management Office at (416) 965-5788.

Paper No.

Page No.

INTRODUCTION

PART A: AIR QUALITY RESEARCH:

FEATURE PAPERS

- A **AN OVERVIEW OF ALBERTA ENVIRONMENT'S DEPOSITION
RESEARCH PROGRAM** 1
H.P. Sims: Director, Alberta Environment's
Research Management Division, Alberta, Canada.
- B **MULTIMEDIA ANALYSIS AND ASSESSMENT OF
ENVIRONMENTAL TOXIC AND CARCINOGENIC SUBSTANCES** ... 29
R. Harkov: Office of Science and Research,
New Jersey Dept. of Environmental Protection,
New Jersey, U.S.A.

SESSION PAPERS

- 1 **THE RAPID SCREENING OF MUNICIPAL REFUSE
INCINERATOR FLYASH AND STACK GAS FOR PCDD/
PCDF USING A TRANSPORTABLE TANDEM MASS
SPECTROMETER (GC/MS/MS) SYSTEM** 45
B. Shushan¹, A. Ngo¹, V. Ozvacic², G. Wong²,
G. DeBrou², B. Bobbie², R. Clement²,
S. Thorndyke³ and B. Chittum⁴. 1-SCIEX,
2-Environment Ontario, 3-ORF, 4-Willington
Consultants.
- 2 **RETROSPECTIVE CORRELATION SPECTROSCOPY
AND ITS APPLICATION TO ATMOSPHERIC MONITORING** 59
R.W. Nicholls, M. Amani, M. Mandelman and
W. Morrow, York University, Toronto, Ontario.
- 3 **MEASUREMENT OF ATMOSPHERIC CONSTITUENTS BY
TUNABLE DIODE LASER ABSORPTION SPECTROMETRY** 64
H.I. Schiff, York University, Toronto, Ontario.
- 4 **UPTAKE, DISTRIBUTION AND CLEARANCE
OF SOLUBLE AEROSOLS IN THE HUMAN
RESPIRATORY SYSTEM** 81
W.J. Megaw¹ and J.F. Hicks². 1-York University,
Toronto, and 2-Environment Ontario.
- 5 **EXPERIMENTALLY DETERMINED MUTATION
RATES IN LUNG AS AN AIR QUALITY
STANDARD** 92
J. Heddle, A. Bouch, C. Couch, H. Kaul,
J. Gingerich and K. Jain, York University,
Toronto, Ontario.

<u>Paper No.</u>		<u>Page No.</u>
6	THE HAMILTON STUDY: EFFECTS OF FINE PARTICLES ON THE RESPIRATORY HEALTH OF SCHOOL CHILDREN	106
	L.D. Pengelly, A. Kerigan, C. Goldsmith, W. Furlong and S. Toplack, McMaster University, Hamilton, Ontario.	
7	BIOLOGICAL MONITORING OF ENVIRONMENTAL GENOTOXICITY	134
	M. Petras, J. Norsworthy, M. Vrzoc, and K. Hill, University of Windsor, Windsor, Ontario.	
8	FIELD AND LABORATORY VALIDATION OF A HIGH-VOL DENUDER FOR MINIMIZING PAH OXIDANT REACTIONS	177
	C.S. Davies ¹ , S. Guerin ¹ , J. Marr ² and M. Quilliam ² . 1-Concord Scientific Corp., 2-McMaster University, Ontario.	
9	A PARTICLE-SIZE SPECIFIC ELEMENTAL MASS BALANCE FOR APPORTIONMENT OF AMBIENT AEROSOL SAMPLED WITH MULTISTAGE FRACTIONATORS	196
	R.E. Jervis and T. Pringle, University of Toronto, Toronto, Ontario.	
45	MUTAGENICITY OF COMPLEX MIXTURES OF PAHS' IN AMBIENT AIR PARTICULATE MATTER	206
	A.S. Raj and M. Katz, York University, Toronto, Ontario.	
46	DOSE - RESPONSE STUDIES OF GASEOUS POLLUTANTS OF FOOD CROPS	219
	D.P. Ormrod and J. Petite, University of Guelph, Guelph, Ontario.	
47	PRODUCTION OF OZONE INSENSITIVE WHITE BEAN VARIETIES	242
	T.E. Michaels, University of Guelph, Guelph, Ontario.	
48	NICKEL CARBONYL AMBIENT MONITOR	249
	D.R. Hastie and H.I. Schiff, York University, Toronto, Ontario.	
49	ELEMENTAL COMPOSITION OF AIR PARTICULATES INSIDE AND OUTSIDE A BUILDING	263
	P. Harvey, J.D. McArthur and G. Palmer, Queen's University, Toronto, Ontario.	

Paper No.

Page No.

50	STUDY OF THE THERMAL REACTIONS OF PCDD ON FLYASH PARTICLES UNDER INCINERATOR CONDITIONS	277
	L.C. Dickson and F.W. Karasek, University of Waterloo, Waterloo, Ontario.	
51	CONTINUOUS EMISSION MONITORING FOR TOTAL HYDROCARBON AT SEWAGE SLUDGE INCINERATORS	305
	J. Kosch, AMKO Systems Inc., Thornhill, Ontario.	
52	STUDY OF THE SPATIAL DISTRIBUTION OF THE IMPACT OF SUDBURY SMELTING EMISSIONS	314
	E.A. McBean, J. Byrne, J. Donald and G. Farquhar, University of Waterloo, Waterloo, Ontario.	
53	CHARACTERIZATION OF BUILDING WAKE EFFECTS AT DARLINGTON NUCLEAR GENERATING STATION USING SULPHUR HEXAFLUORIDE AS A TRACER	330
	G. Ogram ¹ , H. Sahota ² and P.K. Misra ² . 1-Ontario Hydro, 2-Environment Ontario.	

PART B: WATER QUALITY RESEARCH

FEATURE PAPERS

A	PREDICTIVE MODELS IN HAZARD ASSESSMENT OF GREAT LAKES CONTAMINANTS OF FISH	1
	Dora R. May Passino: U.S. Fish and Wildlife Service, National Fisheries Centre - Great Lakes, Ann Arbor, Michigan, U.S.A.	
B	CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTE WATER TREATMENT PLANTS	27
	Henryk Melcer: Biological Processes Section, Wastewater Technology Centre, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario, Canada.	

SESSION PAPERS

10	TRACE ORGANIC CONTAMINANT REMOVAL FROM DRINKING WATER	52
	J. Hilton, MacLaren Plansearch Inc., Toronto, Ontario.	
11	THE ROLE OF ORGANIC CARBON IN CONTROLLING THE OCCURRENCE OF DENITRIFICATION IN GROUNDWATER	67
	R.C. Starr and R.W. Gillham, University of Waterloo, Waterloo, Ontario.	

<u>Paper No.</u>		<u>Page No.</u>
12	REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO, 1980 TO 1985 J. McD. Robertson, H. Chan and I. Fyfe, University of Western Ontario, London, Ontario.	82
13	ORGANIC CONTAMINANT STRUCTURE - PROPERTY - TOXICITY RELATIONSHIPS FOR AQUATIC ORGANISMS S. Abernethy and D. Mackay, University of Toronto, Toronto, Ontario.	113
14	EFFECT OF LEAD, CADMIUM AND MERCURY ON THE TISSUE OF YOUNG FISH AND RATS: DEVELOPMENT OF BIOINDICATOR D.M. Nicholls, R. Angelow, K. Tiechert-Kuliszewska and G. Girgis, York Univesity, Toronto, Ontario.	138
15	IN-SITU ASSESSMENT OF MIXED COPPER AND ZINC IMPACTS ON WHITE SUCKER (<i>Castastomus Commersoni</i>) POPULATIONS IN SEVERAL NORTHERN ONTARIO LAKES: AN EVALUATION OF THE ENVIRONMENTAL HEALTH APPROACH TO VALIDATING WATER QUALITY CRITERIA K.R. Munkittrick and D.G. Dixon, University of Waterloo, Waterloo, Ontario.	165
16	THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS B. Clark, S. Salenicks, J. Glynn Henry and D. MacKay, University of Toronto, Toronto, Ontario.	176
17	TOXICITY OF PENTACHLOROPHENOL TO ZOOPLANKTON N.K. Kaushik and G. Stephenson, University of Guelph, Guelph, Ontario.	192
18	DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY FOR THE DETECTION OF TRACE CONTAMINANTS WITHIN WATERS OF THE ONTARIO GREAT LAKES REGION A. Melkic, E. Greece and D. Lewis, Integrated Explorations Ltd., Guelph, Ontario.	205
54	EVALUATION OF DATA ON THE EFFECTS OF HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION ON THE INCIDENCE OF MICRO-ORGANISMS OF PUBLIC HEALTH SIGNIFICANCE IN RECEIVING WATERS M. Palmer, Gore & Storrie Ltd., Toronto, Ontario.	219
55	LISTOWEL ARTIFICIAL MARSH TREATMENT PROJECT J. Herskowitz, S. Black and W. Lewandowski, Ministry of the Environment, Toronto, Ontario.	244
56	A LOW PRESSURE HYDROCYCLONE FOR USE IN SEWAGE TREATMENT J.D. Boadway, Queen's University, Kingston, Ontario.	267

<u>Paper No.</u>		<u>Page No.</u>
57	THE EFFECTS OF RURAL AND SUBURBAN DEVELOPMENT ON SURFACE WATER QUALITY IN FIVE SELECTED SUBWATERSHEDS ON THE UPPER HUMBER RIVER B. Hindley, R. Hubbard and S. Maude, Metro Toronto Conservation Authority, Toronto, Ontario.	294
58	HUMBER RIVER/BLACK CREEK: DETAILED BACTERIOLOGICAL WATER QUALITY STUDY EXAMINING THEIR IMPACT OF SEDIMENT AND SURVIVAL TIMES P.L. Seyfried and E. Harris, University of Toronto, Toronto, Ontario.	347
59	FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND PHOSPHORUS MANAGEMENT IN SHALLOW IMPOUNDMENT P. McKee, K. Clarke-Whistler and G. Gaspardy, Beak Consultants Ltd., Toronto, Ontario.	392
60	TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE EFFECTS OF DREDGED SEDIMENT DISPOSAL IN PRIMARY PRODUCTION AND PHOSPHORUS KINETICS IN OPEN WATERS C. Ewing and C. Nalewajko, University of Toronto, Scarborough, Ontario.	415
61	STOCHASTIC ESTIMATION OF AMBIENT WATER QUALITY IN THE THAMES RIVER V.A. Graham, T.E. Unny and L. Logan, University of Waterloo, Waterloo, Ontario.	438
62	OTTAWA RIVER NUCLEAR SPILL CONTINGENCY MODEL DEVELOPMENT: PHASE II T. Gowda, M. Palmer, C. Arnoldi and R. Jarvis, Gore & Storrie Ltd., Toronto, Ontario.	467

PART C: LIQUID & SOLID WASTE RESEARCH

FEATURE PAPERS

A	HAZARDOUS WASTE DESTRUCTION: AN OVERVIEW OF APPROACHES AND SHORTCOMINGS E. Timothy Oppelt: Thermal-Destruction Branch, Alternative Technologies Division, U.S.-EPA, Cincinnati, Ohio, U.S.A.	1
B	AN OUTLINE OF U.S.-EPA RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTE Norbert Schomaker: Hazardous Waste Engineering Research Lab., US-EPA, Cincinnati, Ohio, U.S.A.	26

Paper No.

Page No.

SESSION PAPERS

19	ASSESSMENT OF A PROTOTYPE SYSTEM FOR PYROLYSIS OF REFUSE DERIVED FUEL	38
	S.J. Thorndyke, Ontario Research Foundation, Mississauga, Ontario.	
20	MUNICIPAL SOLID WASTE FEASIBILITY OF GASIFICATION WITH PLASMA ARC	63
	G.W. Carter, Resorption Canada Ltd., Ottawa, Ontario.	
21	SEWAGE SLUDGE COMPOST AS TURF FERTILIZER	78
	J.L. Eggens, Ontario Agricultural College, University of Guelph, Guelph, Ontario.	
22	WASTE MANAGEMENT PLANNING FOR PHARMACEUTICAL INDUSTRY - PHASE I: INVENTORY AND DATA COLLECTION	85
	R. Makhija and R. Stairs, Trent University, Peterborough, Ontario.	
23	DEVELOPMENT OF GUIDELINES FOR THE UTILIZATION OF INDUSTRIAL WASTE IN BACKFILL AND CONSTRUCTION APPLICATIONS	94
	G. Zukovs, Canviro Consultants Ltd., Toronto, Ontario.	
24	NUMERICAL AND LABORATORY MODELLING OF TWO-PHASE FLOW IN POROUS MEDIA: 1 - TWO-PHASE GASEOUS FLOW, 2 - TWO-PHASE LIQUID FLOW	117
	G. Farquhar, E. McBean, J. Byrne, W. Abbott and R. Kell, University of Waterloo, Waterloo, Ontario.	
25	DEVELOPMENT OF POLYSULFIDE TECHNOLOGY FOR TREATMENT OF CONCENTRATED SPENT CYANIDE LIQUORS ...	144
	J.J. Gaczarczyk, University of Toronto, Toronto,	
26	TREATMENT OF LANDFILL LEACHATE BY SPRAY IRRIGATION	175
	R. McBridge, A.M. Gordon, P. Groenvelt, T. Bates and K. King, University of Guelph, Guelph, Ontario.	
27	CO-DISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTES: PART II	192
	D. Kirk and M. Lau, University of Toronto, Toronto, Ontario.	
63	HAZARDOUS ORGANIC CHEMICALS IN GROUNDWATER AT ONTARIO LANDFILLS.	206
	J.F. Baker and J. Cherry, University of Waterloo, Waterloo, Ontario.	

Paper No.

Page No.

64	DISPERSION OF THE STOUFFVILLE CONTAMINANT PLUME	229
	I. Proulx, R.N. Farvolden and E. Frind, University of Waterloo, Waterloo, Ontario.	
65	DEVELOPMENT OF DESIGN CRITERIA FOR OPTIMAL RECOVERY OF LEACHATE UNDER SANITARY LANDFILLS	243
	L. Arnaud, E. Frind, R. Farvolden and R. Gillham, University of Waterloo, Waterloo, Ontario.	
66	AN INVESTIGATION INTO THE REDOX CONDITIONS OF A LANDFILL LEACHATE PLUME CONTAINING VOLATILE ORGANICS, GLOUCESTER, ONTARIO	272
	L. Elliott, J. Develin, F. Michaels and W. Gorman, Queen's University, Kingston, Ontario.	
67	EFFECTS OF INCREASING AMOUNTS OF NON-POLAR ORGANIC LIQUIDS IN DOMESTIC WASTE LEACHATE ON THE HYDRAULIC CONDUCTIVITY OF CLAY LINERS IN SOUTHWESTERN ONTARIO	294
	R.M. Quigley and F. Fernandez, University of Western Ontario, London, Ontario.	
68	ASSESSMENT OF CONTAMINANT MIGRATION FROM INDUSTRIAL SOURCES DISCHARGING TO THE WELLAND RIVER	315
	M. Dickman, P. Hayes and I. Brindle, Brock University, St. Catharines, Ontario.	
69	EVALUATION OF CONTAMINANT VELOCITY GROUNDWATER IN LOW PERMEABILITY FRACTURE SHALE	338
	E. Sudicky, R. Blackport and J. Cherry, University of Waterloo, Waterloo, Ontario.	
70	GEOMECHANICAL INVESTIGATION OF NEAR-SURFACE FRACTURES IN CLAY TILLS	349
	M. Dusseault and A. Vorauer, University of Waterloo, Waterloo, Ontario.	
71	ORIGINS OF ELEVATED CHLORIDE CONCENTRATIONS IN GROUNDWATER SYSTEMS	376
	P.E. Pilon and K.W.F. Howard, University of Toronto, Scarborough, Ontario.	

PART D: ANALYTICAL METHODS

FEATURE PAPERS

A	TRENDS IN MULTI-ELEMENT ANALYSIS: THE ROLE OF ICP-MS IN ENVIRONMENTAL APPLICATIONS	1
	Barry French, Institute for Aerospace Studies, University of Toronto, Toronto, Ontario, Canada.	

Paper No.

Page No.

B	DETECTION OF HYDROXYLATED NITRO-POLYNUCLEAR AROMATIC HYDROCARBONS AND KETONES IN AN AMBIENT AIR PARTICULATE EXTRACT USING BIOASSAY-DIRECTED FRACTIONATION	31
	Marcia G. Nishioka and Corrine C. Howard, Analytical Chemistry Section, Battelle Columbus Division, Columbus, Ohio, and Joellen Lewtas, U.S. - EPA, North Carolina, U.S.A.	

SESSION PAPERS

28	DIRECT SOLID SAMPLE ANALYSIS WITH THE DIRECT SAMPLE INSERTION DEVICE, PROMISE AND PROBLEMS	64
	E. Salin and R.L. Sing, McGill University, Montreal, Quebec.	
29	SCREENING METHODS FOR AIR AND WATER SAMPLES: APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS) TO ELEMENTAL ANALYSIS	74
	J. Van Loon and B. French, University of Toronto, Toronto, Ontario.	
30	DEVELOPMENT OF SELENIUM ANALYSIS METHODOLOGY AT NG/L LEVELS FOR SOFT WATERS SUBJECT TO ACIDIC PRECIPITATION	97
	L.M. Brown and J. Wehr, University of Western Ontario, London, Ontario.	
31	EVALUATION AND OPTIMIZATION OF A TOC ANALYZER USING UV - PERSULPHATE DIGESTION	111
	R.D. Evans, Trent University, Peterborough, Ontario.	
32	DEVELOPMENT OF AN ULTRASONIC NEBULIZER FOR STABLE AND REPRODUCTIVE PRODUCTION OF AEROSOLS FOR ATOMIC SPECTROMETRIC ANALYSIS	112
	J.C. Van Loon, University of Toronto, Toronto, Ontario.	
33	DEVELOPMENT OF RECOMBINANT DNA PROBES TO DETERMINE THE ORIGIN OF FECAL STREPTOCOCCI AT THE TORONTO AREA BEACHES	133
	W.C. Bradbury, M.A. Marko, L. Papageorgiou, D. Leight and D. Rego, University of Toronto, Toronto, Ontario.	
34	PLANT BIOASSAYS FOR THE DETECTION OF ENVIRONMENTAL MUTAGENS	147
	Wm. F. Grant, McGill University, Montréal, Québec.	
35	A BIOLOGICAL INDICATOR SYSTEM TO IDENTIFY GENOTOXICITY OF IN-PLACE POLLUTANTS	167
	D.R. Hart, J. Fichko, M. Brinkman and P. McKee, IEC Beak Consultants Ltd., Mississauga, Ontario.	

Paper No.

Page No.

36	FRESHWATER CLAMS AS MONITORS OF VARIATION IN ENVIRONMENTAL ACIDITY AND TRACE METAL LEVELS	189
	R.H. Green, S. Hinch and R. Bailey, University of Western Ontario, London, Ontario.	
72	ANALYSIS OF DIOXINS AND FURANS IN FISH AND OTHER BIOTA	215
	F.W. Karasek, T. Thompson, D. Schelenberg and K. Naikwadi, University of Waterloo, Ontario.	
73	DEVELOPMENT OF COST-EFFECTIVE PROTOCOL FOR ROUTINE ANALYSIS FOR TRACE ORGANIC CONTAMINANTS IN MUNICIPAL WPCP RAW SEWAGE AND FINAL EFFLUENT	234
	C. Chan ¹ , J. Martin ¹ , P. Pond ¹ , G. Rees ² , and T. Ho ² . 1-Mann Testing Labs. Ltd., 2-Environment Ontario.	
74	APPLICATION OF GC HELIUM MICROWAVE PLASMA DETECTION TO THE RAPID SCREENING OF CHEMICAL WASTE	255
	M. Danszinger, Barringer Magenta Ltd., Rexdale, Ontario.	
75	DEVELOPMENT OF METHODS SUITABLE FOR THE USE IN THE AMES SALMONELLA MUTAGENICITY ASSAY FOR THE COLLECTION OF ORGANICS PRESENT IN GROUNDWATER AND LANDFILL SITE MATRIX MAERIALS	271
	G.H. Thomas, A. Horton and K. Matsummura, Ontario Research Foundation, Mississauga, Ontario.	
76	SYNTHESIS OF OXYGEN AND SULPHUR PAHS OF INTEREST IN ENVIRONMENTAL POLLUTION	294
	E. Lee-Ruff and F. Ablenas, York University, Toronto, Ontario.	
77	DEVELOPMENT OF A ROBOTIC WORKSTATION FOR THE ROUTINE ANALYSIS OF ORGANICS IN BIOLOGICAL TISSUES USING ACID DIGESTION AND SOLVENT EXTRACTION METHOD	298
	C. Chan ¹ , J. Martin ¹ , G.Ladwig ¹ , G. Rees ² , and G. Crawford ² . 1-Mann Testing Labs Ltd., 2-Environment Ontario.	
78	SEPARATION AND IDENTIFICATION OF ORGANIC COMPOUNDS IN EXTRACTS OF AIR PARTICULATES BY HPLC AND GC/MS	331
	K.P. Naikwadi, G. Charbonneau and F.W. Karasek, University of Waterloo, Waterloo, Ontario.	

Paper No.

Page No.

79	QUANTITATIVE DETERMINATION OF SELECTED PAHS' BY SHPOL'SKII AND JET-COOLED SPECTROSCOPY	355
	C.M. Sadowski, J. Lai, H. Malle, S. Filseth and F. Morgan, York University, Toronto, Ontario.	
80	NEW SYNTHETIC METHODOLOGY FOR THE EXPEDIENT PROVISION OF PURE PAH ANALYTICAL STANDARDS	384
	V.A. Snieckus, University of Waterloo, Waterloo, Ontario.	

PART E: ENVIRONMENTAL ECONOMICS

FEATURE PAPER

A	THE ENVIRONMENT OF ECONOMICS - PAST PRESENT AND FUTURE ROLES OF ECONOMICS IN ENVIRONMENTAL MANAGEMENT	1
	Clifford Russell, Director, Institute for Public Policy Studies, Vanderbilt University, Nashville, Tennessee, U.S.A.	

SESSION PAPERS

37	ABATEMENT COST FUNCTIONS - THE WORKHORSE OF ENVIRONMENTAL MANAGEMENT	18
	J. Donnan, C. Griffith, S. Glover and M. Dandele, Policy & Planning Branch, Ministry of the Environment, Toronto, Ontario.	
38	MEASURING THE SOCIAL COSTS OF ELECTRICAL EXPORTS AND COST RECOVERY OPPORTUNITIES OF ENVIRONMENTAL PROTECTION OF ONTARIO HYDRO	39
	W. Wianko and B. Green, Ontario Hydro, Toronto, Ontario.	
39	QUÉBEC'S EXPERIENCE WITH THE ECONOMIC EVALUATION OF ENVIRONMENTAL REGULATIONS - WHAT LESSONS HAVE BEEN LEARNED	65
	C. Sauvé, Ministère de l'Environnement, Sainte-Foy, Québec.	
40	3M'S POLLUTION PREVENTION PAYS PROGRAM	77
	A.G. Mills, 3M Canada Inc., London, Ontario.	
41	THE BENEFITS OF REDUCING LEAD IN U.S. DRINKING WATER	87
	R. Levin, U.S.-EPA, Washington, D.C., U.S.A.	

Paper No.

Page No.

42	ECONOMIC EFFECTS OF REDUCED FOREST GROWTH IN THE UNITED STATES' FOREST ECONOMY AND ON CANADIAN-U.S. LUMBER TRADE	112
	J.M. Callaway, Jr., Battelle Northwest Labs, Richland, Washington, U.S.A.	
43	SOME ECONOMICS OF THE GRAND CANAL	129
	A. Muller, Department of Economics, McMaster University, Hamilton, Ontario.	

Predictive Models in Hazard Assessment of Great Lakes
Contaminants for Fish¹

Dora R. May Passino

U. S. Fish and Wildlife Service

National Fisheries Center-Great Lakes

Ann Arbor, Michigan 48105

U.S.A

Key words: Structure-Activity Relationships, QSAR, Daphnia, Acute Toxicity,
Linear Solvation Energy Relationships.

ABSTRACT

A hazard assessment scheme was developed and applied to predict potential harm to aquatic biota of nearly 500 organic compounds detected by gas chromatography/mass spectrometry (GC/MS) in Great Lakes fish. The frequency of occurrence and estimated concentrations of compounds found in lake trout (Salvelinus namaycush) and walleyes (Stizostedion vitreum vitreum) were compared with available manufacturing and discharge information. Bioconcentration potential of the compounds was estimated from available data

¹Contribution 670, National Fisheries Center-Great Lakes, Ann Arbor, Michigan 48105, U.S.A.

or from calculations of quantitative structure-activity relationships (QSAR). Investigators at the National Fisheries Center-Great Lakes also measured the acute toxicity (48-h EC50's) of 35 representative compounds to Daphnia pulex and compared the results with acute toxicity values generated by QSAR. The QSAR-derived toxicities for several chemicals underestimated the actual acute toxicity by one or more orders of magnitude. A multiple regression of log EC50 on log water solubility and molecular volume proved to be a useful predictive model. Additional models providing insight into toxicity incorporate solvatochromic parameters that measure dipolarity/polarizability, hydrogen bond acceptor basicity, and hydrogen bond donor acidity of the solute (toxicant).

INTRODUCTION

Natural resource and regulatory agencies are confronted with evaluating a vast and growing number of chemicals that have been detected in the aquatic environment or will be potentially released into it. At the same time, the abundance and diversity of aquatic species has diminished in many areas. In the Great Lakes, chemical contaminants have been suspected of playing a causal role in such fishery resource problems as the increase in the incidence of cancerous tumors in brown bullheads, Ictalurus nebulosus (Baumann 1984), and the reproductive impairment of lake trout, Salvelinus namaycush (Mac et al. 1985). A hazard assessment of the chemicals in the environment and the biota is the first step in evaluating the role of chemicals in fishery resource problems.

As a result of monitoring efforts to detect known and previously unrecognized contaminants in fish from the open waters of the Great Lakes, 476 organic chemicals were tentatively identified in lake trout and walleyes, Stizostedion vitreum vitreum, from the Great Lakes and Lake St. Clair (Hesselberg and Seelye 1982). Detection of such a large array of compounds in fish raises several questions about the sources of the compounds and their potential impacts on fish and other biota, and ultimately about the need for regulatory control of the compounds. Consequently, this long list of chemicals served as a starting point for an assessment of the hazard of various classes of organic chemicals to the aquatic biota in the Great Lakes (Passino et al. 1986; National Fisheries Center-Great Lakes 1986).

At an early stage in the hazard assessment, I discovered that not only were there no consistent data sets for aquatic toxicity or other factors important for assessment of most of these chemicals, but there were no biological data for many of them. Hence, my colleagues and I at the National Fisheries Center-Great Lakes conducted a series of acute bioassays with Daphnia pulex under constant conditions to generate a data set that could be used for comparing classes of chemicals. Even so, the number of data needed to evaluate this huge array of chemicals exceeded the practical capabilities of conducting bioassays. Consequently, other approaches to screening chemicals for hazard to aquatic organisms were clearly required.

A supplemental method for generating experimental data to evaluate chemicals is the use of quantitative structure-activity relationships (QSAR), whereby physical and chemical properties of compounds are used to estimate toxicity, bioaccumulation, and behavior of chemicals in the environment. The origin of this approach can be traced to Crum Brown and Fraser (1868-1869) who suggested that biological activity could depend on aqueous solubility and to Meyer (1899) and Overton (1901) who independently discovered that lipid solubilities of chemicals could predict the narcotic effect of chemicals on organisms. The extensive use of QSAR in modern drug design originated with the pioneering work of Corwin Hansch and his colleagues (Hansch and Fujita 1964; Hansch 1971), which led to the development of many basic models useful to toxicologists. More recently aquatic toxicologists and chemical regulatory agencies such as the U.S. Environmental Protection Agency (USEPA) have screened environmental chemicals with QSAR models (Kaiser 1984; Kamlet 1986); however, the data available to verify the models and their predicted values are notably

sparse. The QSAR models for aquatic toxicology and hazard assessment are still in their early stages of development.

The QSAR models most often applied in aquatic toxicology depend on solubility of chemicals in water or their lipophilicity as usually measured by the partitioning (P) of the chemical between water and octanol (Dearden 1985). Several solubility terms, including molecular weight (MW) and molecular volume (MV), which affect the bioaccumulation of chemicals in aquatic organisms (Neely et al. 1974), can be related to toxicity either by simple linear regression or multiple linear regression. The generalized empirical equation of Hansch (Könemann 1981) included a square of the partitioning coefficient as well as terms relating to acid dissociation and steric parameters of the chemicals (solutes).

Kamlet et al. (1986a; 1986b) recently demonstrated that many "pharmacological and toxicological properties that depend on solute-solvent interactions can be correlated, rationalized and predicted in terms of a single generalized linear solvation energy relationship of simple and conceptually explicit form"(Kamlet et al. 1986b). Solubility and solvent-dependent properties, XYZ, including toxicological properties, are well correlated by equations that include linear combinations of free energy or enthalpy contributions of three types of terms (Kamlet et al. 1986c):

$$XYZ = XYZ_o + \text{cavity term} + \text{dipolar term} + \text{hydrogen bonding term(s)} \quad (1)$$

"The cavity term is a measure of the free energy necessary to separate the solvent molecules (overcome solvent-solvent interactions) to provide a suitably sized cavity for the solute.....The dipole term is a measure of the exoergic

effects of solute-solvent, dipole-dipole, dipole-induced dipole, and dispersion interactions. The solute and solvent parameters that influence this term are π_1^* and π_2^* where π^* is the solvatochromic parameter that is a measure of the ability of a compound to stabilize a neighboring charge or dipole by virtue of its dielectric effect....The hydrogen bonding terms describe the exoergic effects of complexation between HBD (hydrogen bond donar) solvents and HBA (hydrogen bond acceptor solutes), denoted as α_1 and $(\beta_m)_2$...; α and β are the solvatochromic parameters that characterize the HBD acidity and HBA basicity, i.e., they express the abilities to donate and accept a proton to form a hydrogen bond" (Kamlet et al. 1986c).

The generalized equation given by Kamlet et al. (1986a) may be simplified for the situation dealing with solubility properties of multiple solutes in single solvents (as in the present case); the simplified equation relates specifically to solute parameters:

$$SP = SP_0 + m \frac{V_I}{100} + s\pi^* + a(\alpha_m) + b(\beta_m) \quad (2)$$

Where $V_I/100$ = computer calculated intrinsic (van der Waals) molecular volume (Moriguchi et al. 1976)

π^* = dipolarity/polarizability term

α_m = hydrogen-bond donor acidity term

β_m = hydrogen-bond acceptor basicity term.

The term $V_I/100$ is used so that the parameter measuring the cavity term is of the same order of magnitude as the other independent variables, thus facilitating the comparison of the relative contributions of the terms.

The purposes of the present paper are to (1) present an approach to hazard assessment of chemicals detected in Great Lakes fish, (2) demonstrate

the need for toxicity data sets for hazard assessment, and (3) demonstrate the use of several QSAR models to predict toxicity of several classes of chemicals to Daphnia pulex, a representative freshwater zooplankter from the Great Lakes.

MATERIALS AND METHODS

The 476 chemicals that served as the focal point of this hazard assessment were tentatively identified by gas chromatography/mass spectrometry using a Finnigan 4023 quadrapole GC/MS² with an Incos data system (Passino et al. 1986). After grouping the chemicals into about 50 classes, Passino et al. (1986) developed a provisional hazard ranking of the classes based on available data on aquatic toxicity bioconcentration, occurrence in fish, and potential sources. Because data were sparse for aquatic toxicity--the factor considered most important in evaluating hazard--the National Fisheries Center-Great Lakes (1986) conducted acute toxicity bioassays with Daphnia pulex, using 30 chemicals representative of the 19 classes that were highest in the provisional hazard ranking.

My colleagues and I calculated a revised hazard ranking of classes that incorporated acute toxicity data developed for D. pulex (National Fisheries Center-Great Lakes 1986), information on occurrence and abundance of the chemicals in Great Lakes fish (Hesselberg and Seelye 1982), and potential sources of the chemicals (Passino et al. 1986). Each chemical class was assigned a rank relative to the other classes for each category (toxicity,

²Use of trade names or manufacturer's names does not imply U.S. Government endorsement of commercial products.

occurrence, and source). For each class and category a weighted ratio was calculated as follows:

$$\text{weighted ratio} = (\text{rank}/\text{maximum rank}) \times \text{weight} \quad (3)$$

The weights were selected on the basis of estimated relative contribution of each category to the hazard of the chemicals and on the accuracy of the information for that category. The weighted ratios of each category for a given class were summed to determine a hazard ranking value for each class.

Acute bioassays were completed with D. pulex for 35 representative and related chemicals from the following top-ranked classes for which available toxicity data were deemed inadequate to evaluate the hazard of the classes (National Fisheries Center-Great Lakes 1986; Perry 1986): polyaromatic hydrocarbons (PAHs), alkyl halides, monocyclic and polycyclic alkanes, heterocyclic nitrogen compounds, other nitrogen-containing compounds, and silicon-containing compounds (alkylether silanes). The acute bioassays with D. pulex followed established methods of National Fisheries Center-Great Lakes (1986) and Passino and Novak (1984) with temperature at 20 C in reconstituted hard water.

Passino and Smith (1986) used the following parameters from a QSAR data base as independent variables for regressions of the natural logarithm of the measured acute toxicity (log EC50) to D. pulex: calculated acute toxicity to Daphnia (QSAR log LC50), logarithm of the octanol-water partitioning coefficient (log P), water solubility (Cw), and molecular volume (MV). The molecular volume was the molecular weight of the chemical divided by its liquid density. These QSAR estimates were obtained from the data base of USEPA, Duluth, Minnesota, which is accessible at Montana State University, Center for Data Systems and Analysis. The actions of chemicals on living systems are

better understood in terms of the number of molecules present than in terms of the weight of the chemicals. Hence, Passino and Smith (1986) calculated regressions for concentrations expressed both as μM and mg/L . For the solvatochromic models, I obtained the values for $V_I/100$, π^* , α_m , and β_m from Kamlet (1986a; 1986b; 1986c; personal communication). Linear regression analysis, covariance analysis for class differences, quadratic equations, and multiple regressions were computed with SAS (SAS Institute Inc. 1985).

RESULTS AND DISCUSSION

I focused my attention on estimating the hazard of the highly ranked classes of chemicals and representative chemicals within the classes, rather than on individual chemicals because the identification of the 476 chemicals by GC/MS was only provisional. An initial attempt to confirm the identity of 10 of the 476 chemicals by comparison with standards indicated that the unknowns in the fish shared important structures in common with these standards, but that the unknowns were not identical to the standards (James P. Hickey, National Fisheries Center-Great Lakes, personal communication). Hence, I emphasized the structure-activity relationships for classes and groups of classes of the chemicals. Measured acute toxicities to Daphnia pulex and regressions of toxicities on several properties obtained from the QSAR data base are presented in TABLES 1 and 2. Equations (4), (6), (8), and (10) of TABLE 2 are graphed in FIGURES 1 to 4.

Initial QSAR regression lines included all data. However, certain data were excluded from equations (4) to (11) of TABLE 2 because of problems with either the QSAR estimates or with the bioassays. I did not exclude data

because of suspected lack of fit to a narcosis model. The water solubilities for four heterocyclic nitrogen compounds--nicotine; 2-pyridineethanol; 1-methylpyrrolidine; and 2-amino-4,7(1H,8H)-pteridinedione--and an additional nitrogen-containing compound (1-butylimidazole) ranged from 30,900 to 7,450,000 uM. Because these compounds with high solubilities were generally outliers (possibly because they were acting by a receptor-specific mode of action), I omitted them (on a statistical basis) from regressions of EC50 on water solubility, log P, and log QSAR LC50. Inasmuch as the water solubilities of three silicon-containing compounds--(dodecyloxy)trimethylsilane; (decyloxy)trimethylsilane; and siloxytrimethylcyclohexene--were 1.5 to 4 orders of magnitude below the measured acute toxicities, I considered the acute toxicities questionable and excluded them from the regressions. However, the influence of the carrier solvent, acetone, may have increased the solubility of these compounds. It is also possible that these silicon-containing compounds do not act according to a narcosis model. Predicted acute toxicities to Daphnia (QSAR LC50) were unavailable for six other chemicals; however, predicted toxicities to fathead minnows (Pimephales promelas) were available for three of these so I substituted these values, since QSAR toxicities for Daphnia and fathead minnows usually differed by only about 20% (QSAR data base from USEPA, Duluth, MN).

The above examples illustrate the importance of examining QSAR predictions for reasonableness before using them to establish regression equations or before substituting them into established regression equations to predict toxicity. QSAR data bases should be screened to eliminate values such as water solubilities of $1,000,000 \text{ mg.L}^{-1}$. Regression equations should be examined for outliers and the chemical or biological basis for statistical outliers considered.

Multiple regression analysis of log EC50 (μM) as a function of the four independent variables (TABLE 2) indicated that 76% of the variation could be explained by a regression on water solubility and molecular volume (Equation 12). The fit was not improved significantly ($P > 0.05$) by adding log P and log QSAR LC50 (μM). Water solubility was the single most important independent variable, explaining 71% of the variation (Equation 8).

To examine differences between classes (TABLE 3), I determined that the slopes for all classes were homogeneous. For classes with different intercepts, regressions for individual classes might yield a more accurate predicted EC50, although the regression coefficient could decrease because of the smaller sample size.

Although toxicity is often correlated with log P by a simple linear regression, I examined the quadratic equation that includes the $(\log P)^2$ term, based on the generalized equation of Hansch (Könemann 1981). A plot of the residuals for the simple linear regression showed that the residuals were not randomly distributed, thus violating an assumption of the validity of the simple linear regression. Some investigators have approached the problem of nonlinearity by limiting the equation to log P values below some arbitrary value such as 5 or 6 (Könemann and Leeuwen 1980). When I eliminated toxicants with $\log P \geq 6$, the regression coefficient was lowered ($r^2 = 0.43$). The quadratic equation proved more satisfactory. The following regression was calculated with the same 26 data points from Equation 6:

$$\begin{aligned} \log \text{EC50}(\mu\text{M}) &= -2.47 + 3.60 \log P - 0.58 (\log P)^2 & (14) \\ n &= 26; r^2 = 0.77; s = 1.29 \end{aligned}$$

The regression coefficient ($r^2 = 0.77$) improved over the value ($r^2 = 0.69$) for equation 6. A plot of the residuals of equation 14 indicated a random distribution, thus supporting the assumption that the quadratic equation is a valid model. Equation 14 describes a nonlinear relation in which the toxicity reaches a maximum (FIGURE 5). The biological basis for this curve may be that increased lipophilicity favors transport of the toxicant into the membrane and to target sites up to a certain optimum lipophilicity, as measured by log P, after which point, with increased lipophilicity, the toxicants are sequestered in the membrane and tend less to reach the target sites.

TABLE 4 presents the acute toxicity values of 18 solutes (TABLE 1) to Daphnia pulex and the intrinsic molecular volume and solvatochromic terms for solutes for which values of $V_I/100$, π^* , α_m , and β_m are known or can be estimated. The multiple linear regression for the 18 solutes in TABLE 4 is given by the following equation:

$$EC50(\mu M) = 12.1 - 10.7 V_I/100 - 2.46 \pi^* + 6.62 \beta_m \quad (15)$$

$$n = 18; r = 0.9199; s = 0.85$$

The hydrogen bonding donor acidity term α_m was not significant for this data set. By standards that Kamlet (1986a) applied to other QSAR correlations of equation 2--even if not necessarily by the standards usually applied to correlations of biological properties--the r and SD values of equation 15 represent unsatisfactory goodness of fit. I therefore undertook to examine the outliers in the correlation to ascertain whether nonconformance with equation 15 is due to reactive toxicological behavior, as opposed to nonreactive behavior of solutes fitting a narcosis model. After solutes 5, 11, 16, and 17

were dropped, the new regression for 14 solutes from TABLE 4 was as follows:

$$EC50(uM) = 13.9 - 12.7 V_I/100 - 4.30\pi^* + 15.6 \beta_m \quad (16)$$

$$n = 14; r = 0.9763; s = 0.51$$

This equation shows that increasing solute intrinsic molecular volume and decreasing solute HBA basicity, which lead to lower solubility in water, also lead to greater toxicity (lower EC50 values) of the toxicants, but that higher solute dipolarity/polarizability (π^*), which leads to greater solubility in water, also leads to lower EC50 values. Kamlet et al. (1986a;1986b) observed similar converse effects of solute dipolarity on toxicities to luminescent bacteria and golden orfe fish and feel these observations may have important implications regarding the mechanism of toxicity or narcosis.

Besides correlating QSAR parameters with measured toxicity, Passino and Smith (1986) qualitatively compared measured toxicity with the presence of functional groups on the molecules. Although they tested only 2 to 13 chemicals in each class, certain relations were suggested. The presence and position of methyl groups on PAHs were related to toxicity--e.g., the 48-h EC50 ($mg.L^{-1}$) for naphthalene was 4.66, compared with 0.193 for 2,6-dimethylnaphthalene and 0.506 for 1,3-dimethylnaphthalene (TABLE 1). The most toxic compound--aside from the reference chemical p,p'DDT, which is recognized to act by specific reactive toxicological behavior--was 1,4,9,9-tetramethyloctahydromethanoazulene, which had a bridge carbon as well as four methyl groups. The toxicity of alkyl halides appeared to depend on the particular halide attached ($Cl > Br > I$), chain length (longer-chain compounds were more toxic than shorter-chain compounds), and branching of the chains--e.g., 2-iodobutane was less toxic than 2-iodo-2-methylpropane.

Regression equations, taken together with considerations of the presence and position of key functional groups predicted the acute toxicity of PAHs, alkyl halides, cyclic alkanes, and heterocyclic nitrogen compounds to Daphnia pulex by classical QSAR models. Values for parameters for the solvatochromic model were lacking for these heterocyclic nitrogen compounds. Verification of the relation between acute toxicities to Daphnia and those to fish for chemicals in these classes is needed. Because of possible reactive modes of action, low solubility, or both, Passino and Smith (1986) were not able to apply the QSAR models to silicon-containing compounds or other nitrogen-containing compounds. The regressions discussed in this paper have application to hazard assessment of chemicals that are detected and confirmed as present in fish and other aquatic biota. Although QSAR models for hazard assessment are still primarily a research tool, they should become useful to operations personnel after further development of larger aquatic toxicity data sets to verify the models and further work on the toxicological basis for the models.

ACKNOWLEDGMENTS

I thank Anthony M. Frank for guidance with biometrics, SAS programs, and computer graphics; Dr. Mortimer J. Kamlet, Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland, for introducing me to linear solvation energy relationship; and Marc A. Blouin, Cynthia M. Perry-Sayers, Dr. Jacqueline F. Savino, and Stephen B. Smith for laboratory bioassays.

REFERENCES

- Baumann, P.C. 1984. Cancer in wild freshwater fish populations with emphasis on the Great Lakes. *J. Great Lakes Res.* 10:251-253.
- Crum Brown, A. and Fraser, T.R. 1868-1869. On the connection between chemical constitution and physiological action. I. On the physiological action of salts of the ammonium bases, derived from strychnia, brucia, thebaia, codeia, morphia, and nicotia. *Trans. R. Soc. Edinburgh* 25:151-203 (not seen; cited by Dearden 1985).
- Dearden, J.C. 1985. Partitioning and lipophilicity in quantitative structure-activity relationships. *Environ. Health Perspect.* 61:203-228.
- Hansch, C. 1971. Quantitative structure-activity relationships in drug design. In E. J. Ariens, ed., *Drug Design*, vol. 1, pp. 271-342. Academic Press, New York.
- Hansch, C. and Fujita, A. 1964. Rho, sigma and pi analysis-correlations of biological activity and chemical structure. *J. Amer. Chem. Soc.* 86:1616-1626.
- Hesselberg, R.J. and Seelye, J.G. 1982. Identification of organic compounds in Great Lakes fishes by gas chromatography/mass spectrometry: 1977. Administrative Report No. 82-1. Great Lakes Fishery Laboratory, Ann Arbor, Michigan.
- Kaiser, K.L.E. 1984. *QSAR in Environmental Toxicology*. D. Reidel, Dordrecht, Holland.

- Kamlet, M.J., Doherty, R.M., Veith, G.D., Taft, R.W. and Abraham, M.H. 1986a. Solubility properties in polymers and biological media. 7. An analysis of toxicant properties that influence inhibition of bioluminescence in Photobacterium phosphoreum (the Microtox test). Environ. Sci. Technol. 20:690-695.
- Kamlet, M.J., Doherty, R.M., Taft, R.W., Abraham, M.H., Veith, G.D. and Abraham, D.J. 1986b. Solubility properties in polymers and biological media. 8. An analysis of the factors that influence toxicities of nonelectrolytes to the golden orfe fish (Leuciscus idus melanotus). Environ. Sci. Technol. In press.
- Kamlet, M.J., Doherty, R.M., Abboud, J.-L.M., Abraham, M.H. and Taft, R.W. 1986c. Linear solvation energy relationships: 36. Molecular properties governing solubilities of organic nonelectrolytes in water. J. Pharm. Sci. 75:338-349.
- Könemann, H. 1981. Quantitative structure-activity relationships in fish toxicity studies. Part 1: Relationship for 50 industrial pollutants. Toxicology 19:209-221.
- Könemann, H. and Leeuwen, K. van. 1980. Toxicokinetics in fish: Accumulation and elimination of six chlorobenzenes by guppies. Chemosphere 9:3-19.
- Mac, M.J., Edsall, C.C. and Seelye, J.G. 1985. Survival of lake trout eggs and fry reared in water from the upper Great Lakes. J. Great Lakes Res. 11:520-529.
- Meyer, H. 1899. Lipoidtheorie der Narkose. Arch. Exp. Pathol. Pharmacol. 42: 109-118 (not seen; cited by Dearden 1985).

- Moriguchi, I., Kanada, Y. and K. Komatsu. 1976. Van der Waals volume and the related parameters for hydrophobicity in structure-activity studies. Chem. Pharm. Bull. 24:1799-1806.
- National Fisheries Center-Great Lakes. 1986. Progress in Fishery Research 1984-1985. U.S. Fish and Wildlife Service, National Fisheries Center-Great Lakes, Ann Arbor, Michigan.
- Neely, W.B., Branson, D.R. and Blau, G.E. 1974. Partition coefficient to measure bioaccumulation potential of organic chemicals in fish. Environ. Sci. Technol. 8:1113-1115.
- Overton, E. 1901. Studien über die Narkosen. Gustav Fisher, Jena, Germany.
- Passino, D.R.M., Hesselberg, R.J. and Willford, W.A. 1986. Preliminary identification and hazard ranking of 476 organic compounds in Great Lakes fishes. J. Great Lakes Res. In press.
- Passino, D.R.M. and Novak, A.J. 1984. Toxicity of arsenate and DDT to the cladoceran Bosmina longirostris. Bull. Environ. Contam. Toxicol. 33: 325-329.
- Passino, D.R.M. and Smith, S.B. 1986 Quantitative structure-activity relationships (QSAR) and toxicity data in hazard assessment. In K.L.E. Kaiser, ed., QSAR in Environmental Toxicology. D. Reidel, Dordrecht, Holland. In press.
- Perry, C.M. 1985. The toxicological effects of six heterocyclic nitrogen compounds on Daphnia pulex. M.S. Thesis, Eastern Michigan University, Ypsilanti, Michigan.
- SAS Institute Inc. 1985. SAS Users Guide: Basics, Version 5 Edition. SAS Institute Inc., Cary, North Carolina.

TABLE 1. Chemicals used for calculating QSAR equations. Acute toxicity to *Daphnia pulex* (National Fisheries Center-Great Lakes 1986). Water solubility (calculated values from QSAR data base of U.S. Environmental Protection Agency, Duluth, MN). From Passino and Smith (1986).

Chemical	CAS No.	Formula	48-h EC50 μM	Water solubility μM
Cyclohexane,bromo-	108850	C ₆ H ₁₁ Br	36.6	508
Decane,1-bromo-	112298	C ₁₀ H ₂₁ Br	0.335	0.89
Dodecane,1-chloro-	112527	C ₁₂ H ₂₅ Cl	0.0644	0.07
Butane,2-iodo-	513484	C ₄ H ₉ I	59.2	1470
Cyclohexane,chloro-	542187	C ₆ H ₁₁ Cl	34.1	1040
Hexadecane,1-iodo-	544774	C ₁₆ H ₃₃ I	0.702	0.00
Nonane,1-bromo-	693583	C ₉ H ₁₉ Br	2.61	3.60
Cyclohexane,(3-chloro-1-propnyl)-	55723994	C ₉ H ₁₃ Cl	10.1	660
Cyclopentane,propyl-	2040962	C ₈ H ₁₆	27.8	26.0
Cyclohexane,1,2-dimethyl-,cis-	2207014	C ₈ H ₁₆	28.9	24.6
Cyclohexane,1,2-dimethyl-,trans-	6876239	C ₈ H ₁₆	43.5	24.6
Pinane,-trans-	10281535	C ₁₀ H ₁₈	24.3	11.4
Pyridine,3-(1-methyl-2-pyrrolidinyl)- [Nicotine]	54115	C ₁₀ H ₁₄ N ₂	1.50	141000
2-Pyridineethanol	103742	C ₇ H ₉ ON	112	7450000
Pyrrolidine,1-methyl-	120945	C ₅ H ₁₁ N	24.5	569000
4,7(1H,8H)-Pteridinedione,2-amino-	529691	C ₆ H ₅ O ₂ N ₅	16.40	
Imidazole,1-butyl-	4316421	C ₇ H ₁₂ N ₂	53.0	30900
Phenanthrene	85018	C ₁₄ H ₁₀	1.97	6.57
Fluorene	86737	C ₁₃ H ₁₀	1.28	9.76
Decalin	91178	C ₁₀ H ₁₈	18.0	14.4
Naphthalene	91203	C ₁₀ H ₈	36.4	230
Tetralin	119642	C ₁₀ H ₁₂	18.2	113
Anthracene	120127	C ₁₄ H ₁₀	4.24	0.607
Hydrindan	496106	C ₉ H ₁₆	29.8	39.7
Naphthalene,1,3-dimethyl-	575417	C ₁₂ H ₁₂	4.92	22.9
Naphthalene,2,6-dimethyl-	581420	C ₁₂ H ₁₂	1.24	4.08
Anthracene,2-methyl-	613127	C ₁₅ H ₁₂	0.502	1.46
Naphthalene,decahydro-2,3-dimethyl-	1008806	C ₁₂ H ₂₂	0.242	0.436
Anthracene,9-methoxy-	2395962	C ₁₅ H ₁₂ O	1.90	572
1H-3A,7-Methanoazulene,1,4,9,9-tetramethyloctahydro-	19078354	C ₁₅ H ₂₆	0.0182	0.199
p,p'DDT	50293	C ₁₄ H ₉ Cl ₅	0.00299	0.00876
Silane,dimethyldiethoxy-	78626	C ₆ H ₁₆ O ₂ Si	17.9	42.1
Silane,(dodecyloxy)trimethyl-	6221881	C ₁₅ H ₃₄ OSi	0.703	0.0001
Cyclohexene,siloxytrimethyl-	6651361	C ₉ H ₁₈ OSi	289	
Silane,(decyloxy)trimethyl-	18402103	C ₁₃ H ₃₀ OSi	25.3	0.0035

TABLE 2. Summary of structure-activity regressions of measured acute toxicity of PAHs, alkyl halides, cyclic alkanes, and heterocyclic nitrogens to Daphnia pulex (EC50)^a with several QSAR calculated properties of the chemicals; where QSAR LC50 = calculated toxicity to Daphnia; C_w = water solubility; MV = molecular volume; and the units are indicated as μM or mg·L⁻¹; s = the square root of the mean square error for regression. From Passino and Smith (1986).

Equation No.	Equation
(4)	$\log \text{EC50}(\mu\text{M}) = 0.59 + 0.693 \log \text{QSAR LC50}(\mu\text{M})$ $n = 23; r^2 = 0.44; s = 1.41$
(5)	$\log \text{EC50}(\text{mg}\cdot\text{L}^{-1}) = 0.0192 + 0.609 \log \text{QSAR LC50}(\text{mg}\cdot\text{L}^{-1})$ $n = 23; r^2 = 0.38; s = 1.35$
(6)	$\log \text{EC50}(\mu\text{M}) = 10.5 - 2.03 \log P$ $n = 26; r^2 = 0.69; s = 1.48$
(7)	$\log \text{EC50}(\text{mg}\cdot\text{L}^{-1}) = 8.05 - 1.89 \log P$ $n = 26; r^2 = 0.70; s = 1.33$
(8)	$\log \text{EC50}(\mu\text{M}) = -0.539 + 0.714 \log C_w(\mu\text{M})$ $n = 26; r^2 = 0.54; s = 1.28$
(9)	$\log \text{EC50}(\text{mg}\cdot\text{L}^{-1}) = -1.04 + 0.674 \log C_w(\text{mg}\cdot\text{L}^{-1})$ $n = 26; r^2 = 0.68; s = 1.39$
(10)	$\log \text{EC50}(\mu\text{M}) = 9.15 - 0.0448 \text{ MV}$ $n = 32; r^2 = 0.63; s = 1.54$
(11)	$\log \text{EC50}(\text{mg}\cdot\text{L}^{-1}) = 6.65 - 0.0410 \text{ MV}$ $n = 32; r^2 = 0.63; s = 1.43$
(12)	$\log \text{EC50}(\mu\text{M}) = 3.72 + 0.485 \log C_w(\mu\text{M}) - 0.0208 \text{ MV}$ $n = 26; r^2 = 0.76; s = 1.32$
(13)	$\log \text{EC50}(\text{mg}\cdot\text{L}^{-1}) = 2.89 + 0.435 \log C_w(\text{mg}\cdot\text{L}^{-1}) - 0.0213 \text{ MV}$ $n = 26; r^2 = 0.75; s = 1.24$

^aFrom National Fisheries Center-Great Lakes 1986.

TABLE 3. Summary of covariance tests for differences between classes for the structure-activity regressions between $\log EC_{50}(\mu M)$ and several independent variables (see TABLE 1). Lines under classes indicate no significant differences for intercepts, where Het. N = heterocyclic nitrogens, Alk.X = alkyl halides, Cy. Alk. = cyclic alkanes. From Passino and Smith (1986).

Independent variable	Class differences ^a		Classes sorted	
	Slope	Intercept	$P \geq 0.05$	
$\log QSAR (\mu M)$	NS	*	<u>Alk.X PAHs</u>	Cy.Alk.
$\log P$	NS	*	<u>PAHs Alk.X</u>	Cy.Alk.
$\log C_w (\mu M)$	NS	*	<u>Alk.X PAHs</u>	Cy.Alk.
MV	NS	**	<u>PAHs Het.N</u>	<u>Alk.X Cy.Alk.</u>

^aNS = not significant $P > 0.05$

* = $P \leq 0.05$

** = $P \leq 0.01$

TABLE 4. Data used in correlation of non-reactive toxicological effects on Daphnia pulex with intrinsic molecular volume and solvatochromic parameters.

No. Toxicant	$V_I/100$	π^*	β_m	log EC50 μM
1 Phenanthrene	1.015	0.80	0.20	0.68
2 Naphthalene	0.753	0.70	0.15	3.59
3 2-Methylnaphthalene	1.113	0.76	0.21	-0.69
4 1,3-Dimethylnaphthalene	0.949	0.62	0.17	1.59
5 2,6-Dimethylnaphthalene	0.949	0.62	0.17	0.21
6 Tetralin	0.883	0.50	0.12	2.91
7 9-Methoxyanthracene	1.153	0.93	0.32	0.64
8 Anthracene	1.015	0.80	0.20	1.44
9 Fluorene	0.900	1.00	0.20	0.24
10 1-Chlorododecane	1.324	0.26	0.10	-2.74
11 1-Bromononane	1.079	0.35	0.05	0.96
12 1-Bromodecane	1.177	0.34	0.05	-1.09
13 Propylcyclopentane	0.794	0.02	0	3.37
14 Dimethylcyclohexane	0.794	0.02	0	3.57 ^a
15 Hydrindan	0.884	0.02	0	3.40
16 Decalin	0.982	0.03	0	2.89
17 Chlorocyclohexane	0.688	0.35	0.10	3.53
18 Dimethyldecahydro naphthalene	1.180	0.03	0	-1.42

^aMean of cis and trans isomers

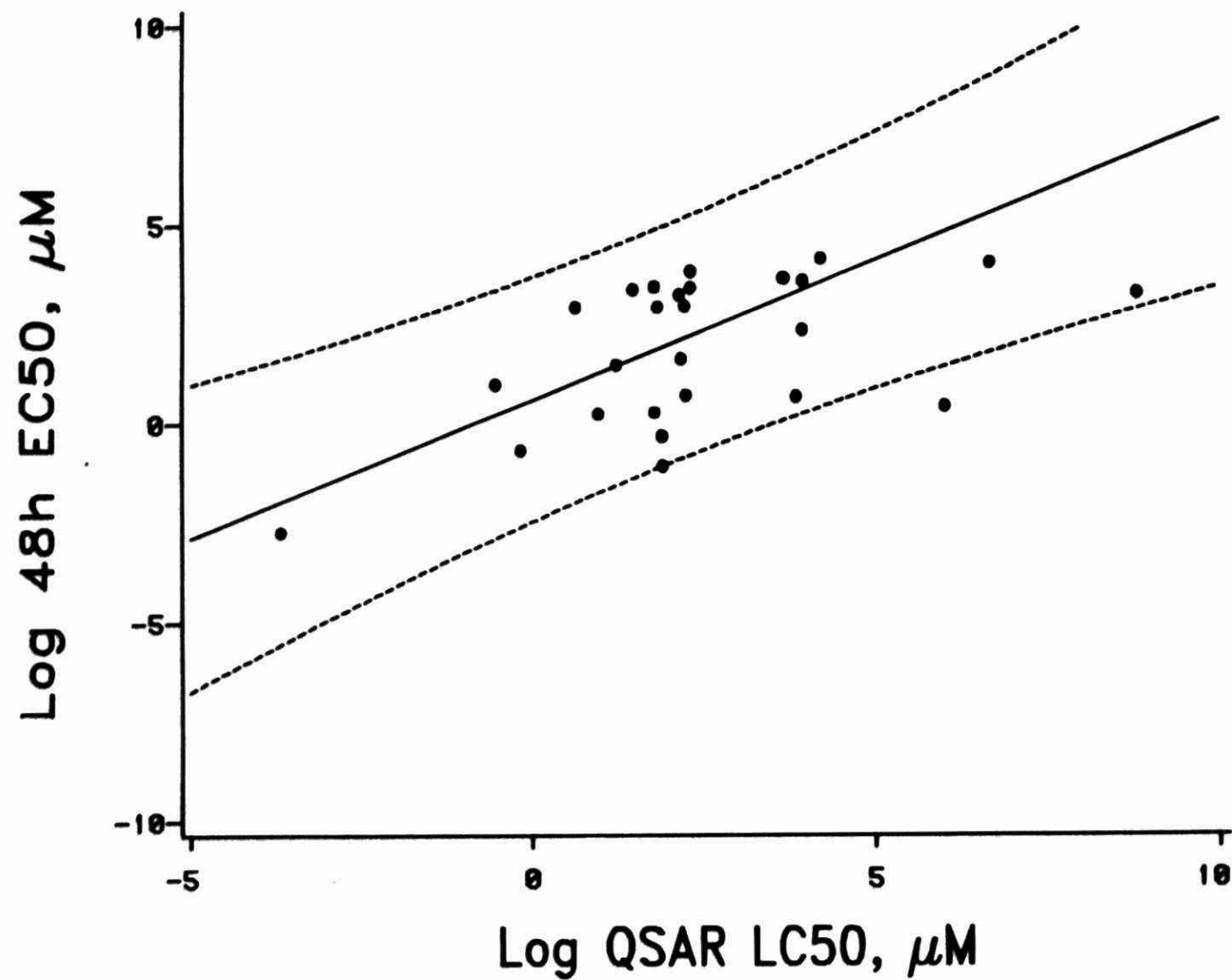


FIGURE 1. Measured acute toxicity to Daphnia pulex of six classes of chemicals versus calculated acute toxicity to Daphnia by QSAR (see TABLE 1).

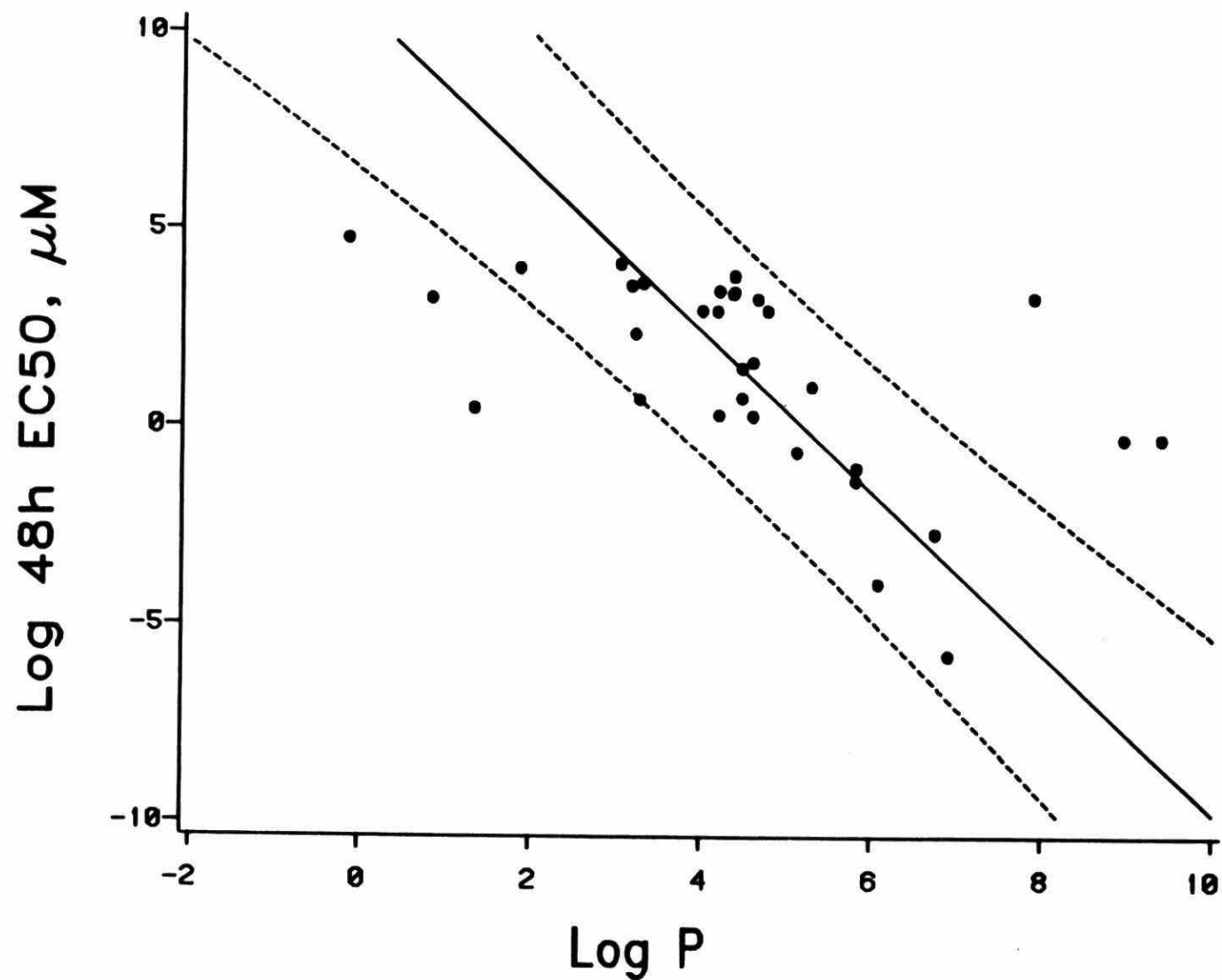


FIGURE 2. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated $\log P$ by QSAR (see TABLE 1).

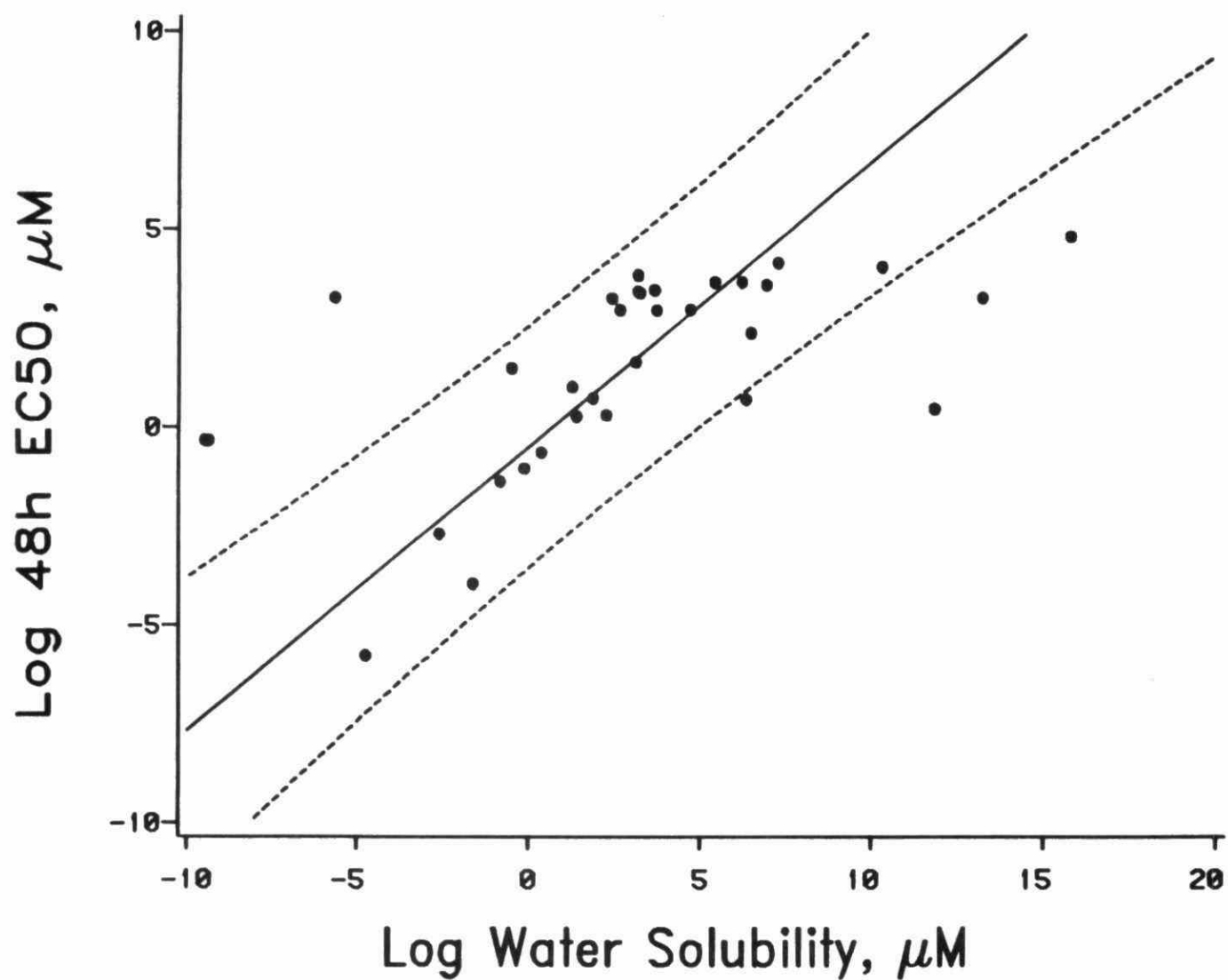


FIGURE 3. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated water solubility by QSAR (see TABLE 1).

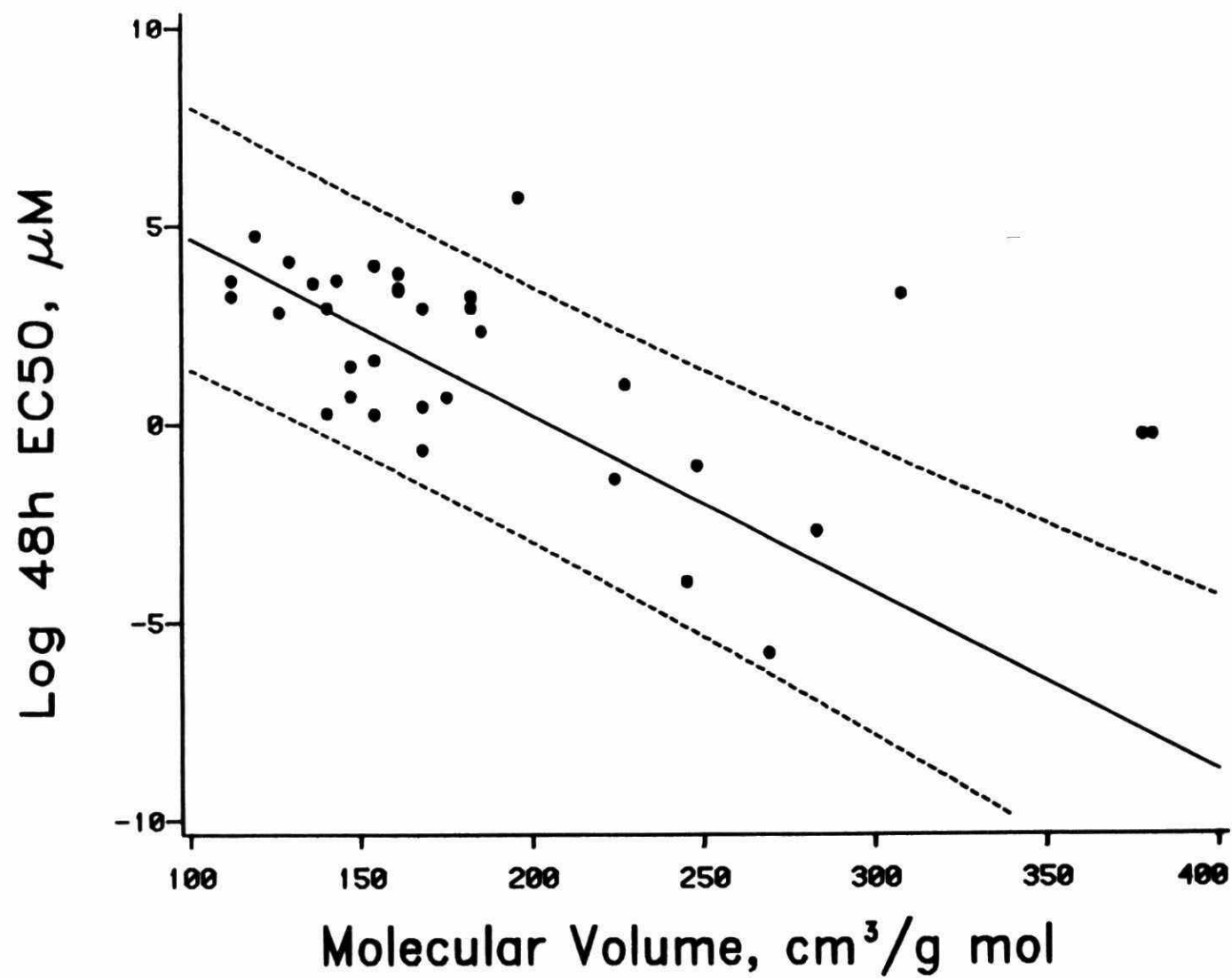


FIGURE 4. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated molecular volume by QSAR (see TABLE 1).

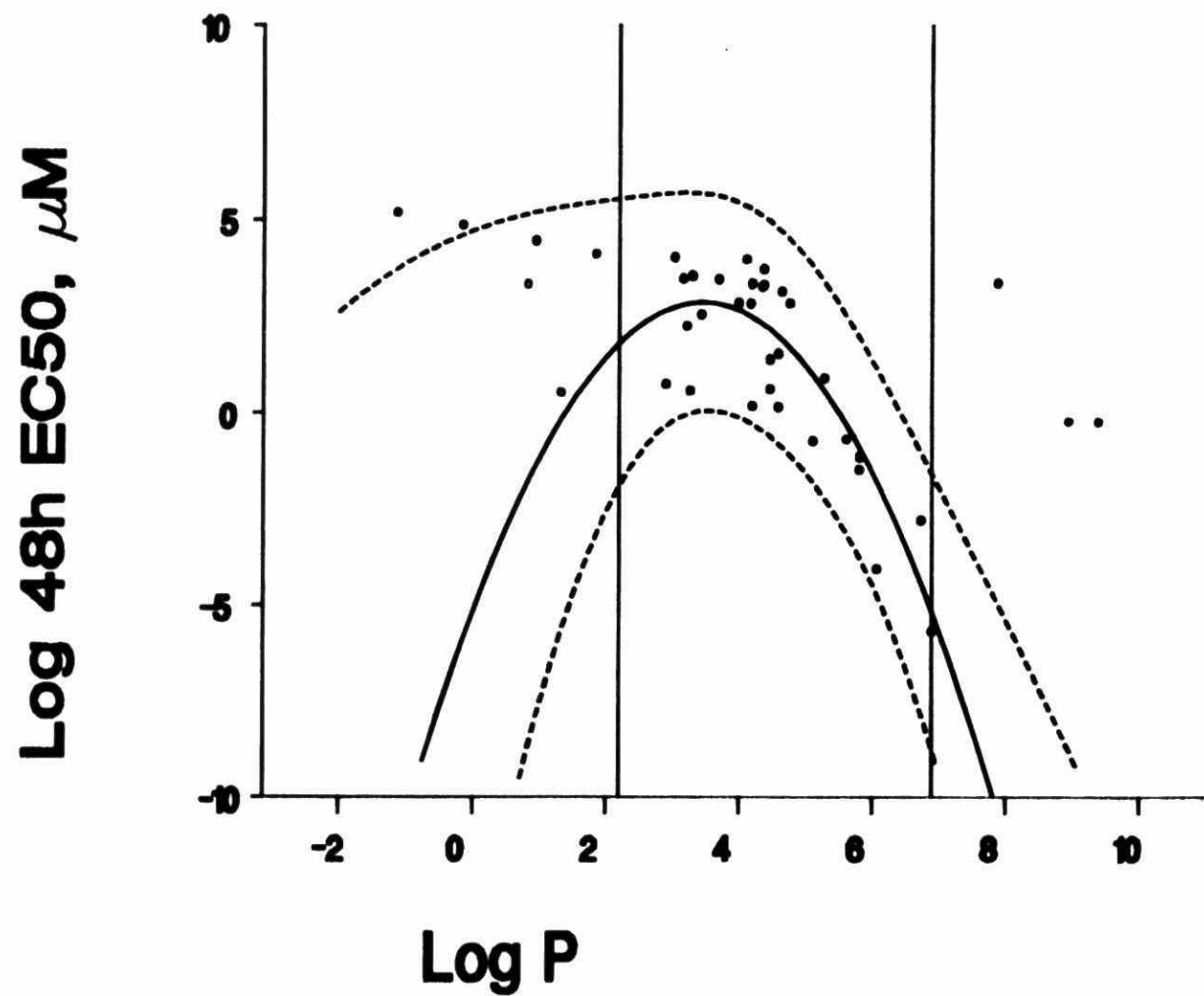


FIGURE 5. Measured acute toxicity to *Daphnia pulex* of six classes of chemicals versus calculated Log P by QSAR (see TABLE 1). The vertical lines approximately delineate the range within which the data points were used for the regression.

**CONTROL OF TOXIC TRACE CONTAMINANTS IN
MUNICIPAL WASTEWATER TREATMENT PLANTS**

Henryk Melcer
Wastewater Technology Centre
Environment Canada
Burlington, Ontario

Ontario Ministry of Environment
Technology Transfer Conference
Toronto, Ontario
8-9 December, 1986

CONTROL OF TOXIC TRACE CONTAMINANTS IN MUNICIPAL WASTEWATER TREATMENT PLANTS

ABSTRACT

Data from more than one hundred municipal wastewater treatment plants were reviewed to determine the most frequently occurring organic and inorganic trace contaminants in treated effluents. Typically, these were volatile chlorinated compounds, phthalate esters and metals. They were found to be removed by volatilization, biodegradation or possibly by adsorption. Manipulation of solids retention time was observed to be a viable approach to controlling the discharge of toxic trace contaminants from sewage treatment plant effluents.

INTRODUCTION

Several major studies were initiated in the late 1970s to measure the removal of trace contaminants in municipal wastewater treatment plants. The U.S. Environmental Protection Agency (USEPA) commissioned the 40 POTW (Publicly-Owned Treatment Works)(1) and the 25 POTW(2) surveys. Although not as large, early Canadian surveys included the St. Clair River Study by the Ontario Ministry of the Environment (MOE)(3) and the Environment Canada (EC) Toxics Study of the Cornwall and Niagara River area municipal wastewater treatment plants(4). Typically, ten to fifteen USEPA priority pollutants were found in effluents from biological wastewater treatment plants at relatively low concentrations of 10 to 30 $\mu\text{g/L}$.

At about the same time, the need for utilizing solids retention time (SRT) control strategies for controlling the removal of trace contaminants in biological wastewater treatment plants was recognized by the scientific community. Manipulation of SRT allowed the treatment plant operator to have control of the microbial growth rate. Key slow-growing organisms that were thought to be responsible for attacking complex molecules could be retained in the biomass. Therefore, provision existed, through SRT control, for addressing those contaminants that were difficult to degrade.

Despite the evidence that trace contaminants were not as prevalent as was originally anticipated, and, that measures existed to control those contaminants that were present in municipal wastewaters, the issue of contaminant emissions continued to receive considerable attention. In Ontario, this can be explained, in part, by our close proximity to the Niagara River and its attendant publicity regarding the discharge and disposal of toxic chemicals. Also, the last five years have seen the introduction of better analytical techniques that have the capability of measuring increasingly lower concentrations of organic compounds in aqueous systems. This relative improvement in measurement has refocused attention on the incidence of toxic trace contaminants in discharges to the Great Lakes. Finally, there has been a rapidly growing public awareness of the fate of anthropogenic compounds and the impact that they may have on our health and the status of the ecosystem. Consequently, not only have further performance assessments been carried out but also many studies have addressed fate of contaminants in municipal sewage treatment plants (STPs). Accordingly, this paper reviews the status of toxic trace contaminant removal in STPs since the time of the landmark surveys of the early 1980s, to those which are currently in progress. Also, studies on the fate of contaminants in biological treatment systems are reviewed.

COMPARATIVE ANALYSIS OF TRACE CONTAMINANT DATA

The majority of data collected to demonstrate the performance of municipal STPs is based on the 126 USEPA priority pollutants. This practice stems from the 1976 consent decree on priority pollutants when the emphasis in the Clean Water Act for water pollution control in the U.S. shifted from regulation based on conventional pollutants alone to regulation based upon conventional and specific toxic pollutants. Considerable analytical chemical methodology development was undertaken to provide protocols that would address those contaminants that were legislated by the Clean Water Act, that is, the priority pollutants. Since that time, it has become evident that many of the priority pollutants are biodegradable and can be removed in municipal STPs. On the other hand, it has also been observed that many commonly used solvent, pesticide and plasticizer chemicals demonstrate toxic and persistent qualities, but are not

included in the list of priority pollutants. They have not been addressed in monitoring or screening procedures until recently, because of the expensive and time-consuming analytical protocol development required to generate methods that are easy to use and give reproducible data. Thus despite the fact that many lists of priority or suspect chemicals have been prepared by regulatory agencies, the most actively reported is that of the USEPA priority pollutants.

There are several reasons why meaningful comparison of data from different surveys is difficult. These include the circumstances under which samples were collected, sampling frequency, method of data reporting and method of sample analysis.

Knowledge of the process operating conditions is very valuable when comparing trace contaminant removal data. This is especially true when comparing laboratory or pilot scale data with field data. The removal of trace contaminants can be affected by the level of biomass acclimation before the commencement of the study. Contaminant removal may also be affected by the method of substrate feed, single or multiple, and by the degree of equilibrium achieved during a study. Other important process considerations are the system hydraulic retention time (HRT), SRT, level of aeration and the feed contaminant concentration. In some cases, the difficulty in comparing removal efficiencies is exacerbated by the presence or absence of chlorination in the treatment sequence. Chlorinated effluents often have elevated concentrations of chlorinated species such as methylene chloride and chloroform. Therefore, removals of these contaminants are often reported as zero or negative. It is rare for researchers to record whether chlorinated or unchlorinated effluent samples were analyzed.

Sampling frequency is not consistent between studies. This discrepancy is often due to the high cost of trace contaminant analysis. Data have been reported based on a single annual sample, on monthly determinations, or, a short series of daily values. The chemical analysis may be carried out on a single grab sample or on a flow-proportioned 24 hr composite sample. Data are then reported as arithmetic or geometric means and medians without any indication whether the values have been corrected for recoveries or not. Various types of

probability distribution functions may be fitted to effluent quality data but no single type has been suitable for all plants. The log-normal distribution is the one that provides an adequate fit most often (5). Sludges may be reported on a wet weight or dry weight basis with no data on the corresponding solids concentration. Execution of a meaningful comparison of statistics is difficult under such circumstances.

The technology of trace contaminant analysis has advanced rapidly during this decade. Levels of detection have been decreasing steadily. As a result of analytical limitations, earlier performance assessments have more values reported as non detected. They were regarded as being zero, or were assigned a value equivalent to the detection level or a value midway between zero and the detection level. Different conclusions may be drawn depending upon how these values were assigned. Although technology has improved the ability to detect contaminants at very low concentrations, there is an inherent difficulty in evaluating contaminant removal efficiencies. This results from the level of uncertainty that still exists with measurement at concentrations near detection limits and leads to considerable variability in effluent data. Conversely, there is difficulty in the measurement of contaminants in influent samples which is attributed to the presence of extraneous organic matter. This organic matrix can interfere with the extraction efficiency of the methylene chloride solvent used to extract the priority pollutants from wastewater samples. This phenomenon can produce a high level of variability in influent contaminant data.

PERFORMANCE ASSESSMENT OF MUNICIPAL STPs FOR REMOVAL OF TOXIC TRACE CONTAMINANTS

Little is known about the human toxicological effect of discharging trace contaminants in STP effluents. The most conservative control strategy possible has been taken in which the lowest concentration of trace contaminants technically achievable is sought. There are limited resources available to address the removal of trace contaminants from STP effluents. Therefore, priorities must be set to utilize these resources in the most cost effective

manner. The contaminants that exist in treated effluents pose a greater potential environmental threat to receiving waters than those in raw wastewaters and, therefore, examination of effluent constituents would appear to warrant a greater priority than an assessment of raw wastewater constituents.

In this review of trace contaminant removal data, attention has been focussed on the USEPA priority pollutants because they form the largest group of trace contaminant data that exists in the literature. An arbitrary basis of comparison was selected, data permitting, in which mean effluent characterization data are presented for those compounds that occurred at concentrations in excess of 1.0 $\mu\text{g/L}$ for more than 50% of the time. A limited number of chlorinated species such as pesticides and PCBs, if they are present, occur generally at much lower concentrations, at one to two orders of magnitude lower than the 1.0 $\mu\text{g/L}$ basis of comparison. Therefore, they are not addressed in this review.

True removal data are difficult to estimate in view of the organic matrix effect on influent sample analysis, the effect of chlorination on effluent constituents and the relative inaccuracy of measurement at detection limits for effluent samples. Therefore, removal data are not presented in this review. Instead, mean influent concentration data are given for the most frequently occurring effluent contaminants for comparison purposes.

On a cautionary note, the protocols used for USEPA priority pollutant analysis will address up to one percent of the organic content of a wastewater sample, treated or otherwise. Many other organic compounds will be present. They make up the remaining part of the organic content of wastewaters. Much of the organic content is made up of large molecular weight compounds some of which are not well defined and about which little is known of their human toxicological effects. Some compounds, however, will be site specific, their occurrence being related to the presence of specific industries that discharge their wastewaters to the STP.

Landmark Studies

These studies were undertaken by the USEPA to address the toxic chemical control measures as defined by the Clean Water Act. They serve as a useful basis of comparison with more recent work. During the period 1978-1981, the USEPA conducted two surveys of trace contaminant removal in STPs. In the first survey, known as the 25 POTW Study, single 24 hr composite samples were taken of the major streams at 25 secondary STPs(2). In a second, more comprehensive survey, the 40 POTW Study, 24 hr composite samples were collected of the major streams at 40 secondary STPs over a period of six consecutive days(1). In the 40 POTW Study, 27 of the 40 STPs met their 30:30/BOD5:TSS discharge permit during the survey.

Both surveys revealed considerable variability in influent concentrations and removal efficiencies of the individual trace contaminants. Very few of the priority pollutants were found on a regular basis in the final effluents in either study. Seven organic compounds and four metals were found above 1 µg/L at least 50% of the time in the 40 POTW Study (Table 1). Seven organic contaminants were similarly found in the 25 POTW Study. Six were the same as those identified in the 40 POTW Study (Table 1). The seventh was diethyl phthalate which occurred 62% of the time. No metal data were collected in the 25 POTW Study.

The Environment Canada Toxics Study(4) identified five organic contaminants that occurred above 1 µg/L at least 50% of the time (Table 1). Samples were composited over seven days at nine STPs and over 24 hr at six STPs in this study. Phenol was found 73% of the time contrary to either the 25 or the 40 POTW Studies. No metal data were collected in the EC study. In the limited screening of the St. Clair River STPs conducted by the Ontario Ministry of the Environment in 1977, all the volatile contaminants listed in Table 1 were also found in the plant effluents(3).

The STPs in the 40 POTW Study were selected to obtain a cross section of secondary treatment processes identified in the 1978 USEPA Needs Survey. These STPs varied in treatment capacity, influent characteristics and industrial flow

TABLE 1 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE 40 POTW STUDY (1)

Contaminant (µg/L)	Influent ¹	Effluent ²
Volatiles		
Chloroform ^{3 4 5}	7	2
Methylene chloride ^{3 4 5}	38	20
Tetrachloroethylene ^{3 4}	23	20
Toluene ⁴	27	10
1,1,1-Trichloroethane ³	29	20
Base Neutrals		
Bis(2-ethylhexyl)phthalate ^{3 5}	27	10
Di-n-butyl phthalate ^{3 5}	4	3
Metals		
Chromium ⁵	105	22
Copper ⁵	132	23
Nickel ⁵	54	38
Zinc ⁵	273	80
Inorganics		
Cyanide ⁵	249	100

¹ Median values for the 40 POTW influent averages. All influent values reported below the detection limit were assumed to be zero (extracted from Table 9(1)).

² The minimum effluent concentrations achieved in the 40 POTW Study at 50% of the POTWs (interpolated from cumulative distributions of effluents(1)).

³ In the list of most frequently found contaminants in the 25 POTW Study(2).

⁴ In the list of most frequently found contaminants in the Environment Canada Toxics Study(4).

⁵ In the list of most frequently found contaminants in the 10 POTW Survey, supplementary to the 40 POTW Study (1).

contributions. A further ten STPs were selected as examples of plants that served one primary industry or industrial category(1). Despite the considerable contribution of contaminants made by the industrial flows to each STP, only one inorganic, four organic and five metal trace contaminants were found above 1.0 µg/L more than 50% of the time in the effluents from these additional STPs (Table 1). Silver was the only one of the ten contaminants that was not the same as those observed in the 40 POTW Study.

Although 50 to 100% removal of some of the priority pollutants was achieved in secondary treatment processes, there were insufficient data to conclude whether this was attributable solely to biodegradation and to what extent adsorption and stripping were significant removal mechanisms. However, some pollutants, such as the polyaromatic hydrocarbons (PAHs), that were not detected in influents, were regularly measured at high levels in corresponding primary and secondary sludges. This suggested that adsorption was taking place and that the sludge was effecting a concentration of the adsorbed compounds. This phenomenon has been documented by Bridle et al.(6)

RECENT PERFORMANCE ASSESSMENTS

Canadian Facilities

An annual inspection of the four Metro Toronto plants is based upon the analysis of grab samples of raw wastewater and final effluent collected at four bi-weekly intervals for each STP. Those contaminants that occurred above 1 µg/L for more than 50% of the time in the final effluent(7) are shown in Table 2. Seven of the twelve organic priority pollutants in Table 2 were common to the 25 and 40 POTW Studies. P-xylene and m-xylene were non-priority organic pollutants that were identified at the Toronto Main and Humber STPs. The STPs were able to effect removals of acid extractable contaminants such as phenol (present in raw wastewaters at concentrations up to 80 µg/L), m-cresol (up to 200 µg/L), and p-cresol (up to 420 µg/L) since they were not detected in the effluents. Neither metal nor conventional plant performance data were collected.

TABLE 2 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN METRO TORONTO STP EFFLUENTS(7)

CONTAMINANT (µg/L)	TORONTO MAIN		NORTH TORONTO		HIGHLAND CREEK		HUMBER	
	Inf.	Eff. ¹	Inf.	Eff. ¹	Inf.	Eff. ¹	Inf.	Eff. ¹
Volatiles								
Chloroform ²	2.5	5.0	3.8	3.1	2.6	4.0	10.7	5.7
Methylene chloride ²	45.1	15.6	8.2	2.6	14.4	14.9	54.8	16.7
Tetrachloroethylene ²	6.6	L	ND ³	L	7.9	11.7	4.4	L
Toluene ²	139	L	1.3	L	347	L	69.0	2.4
1,1,1-Trichloroethane ²	5.6	L	ND	L	59.9	4.5	23.4	L
p- & m-Xylene	63.2	3.0	1.8	L	53.9	L	56.2	2.7
Base Neutrals								
1,2-Dichlorobenzene	12.9	3.0	9.6	L	2.1	2.1	8.7	3.7
1,4-Dichlorobenzene	11.2	5.1	7.0	1.6	11.1	7.0	17.1	6.0
Bis(2-EH)phthalate ²	134	37.9	63.8	14.0	69.4	28.2	85.5	16.4
Diethyl phthalate	10.7	L	9.0	1.8	17.3	L	8.9	L
Di-n-butyl phthalate ²	19.6	2.1	1.6	6.2	32.6	1.9	15.7	5.7
Acid Extractables								
2,4-Dimethylphenol	2.7	3.2	9.4	L	2.0	L	ND	4.4

¹ Mean values for those contaminants present in treated effluents at concentrations greater than 1.0 µg/L for more than 50% of the time. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

² In the list of the most frequently found effluent contaminants in both 25 and 40 POTW Studies.

³ ND - Not detected.

During the period 1981 to 1982, a survey of three Niagara Region STPs was conducted. Sixteen sets of samples were collected for metal analysis; between one to ten were collected for volatile organic contaminant analysis(cited by 8). No conventional plant performance data were collected. A high degree of variability in the data was observed. This was attributed to the limited number of samples and to the fact that so many effluent values were close to detection levels. Contaminants that occurred at more than 1.0 µg/L for more than 50% of the time are presented in Table 3. The three metal contaminants listed in Table 3 were common to the 40 POTW Study (Table 1). Of the ten organic contaminants in Table 3, five were common to both 25 and 40 POTW studies and seven were common to the Metro Toronto Survey. The Welland STP, which is an activated sludge plant, typically had fewer organic contaminants than either the Niagara Falls or the Fort Erie STPs, which are primary treatment facilities. At Fort Erie and Niagara Falls, zinc and cyanide were seen regularly in addition to the ten organic compounds.

Very little data have been published on the performance of primary plants in removing toxic trace contaminants. What data there are, address heavy metal removal and there is a paucity of data on the removal of organic trace contaminants. The USEPA conducted a pilot scale comparative assessment of organic contaminant removal in primary plants (that is, primary sedimentation with and without chemical precipitation compared to primary sedimentation with conventional activated sludge)(9). Considerable pass through of contaminants was observed in the primary plants when compared to the secondary system. The data from the Niagara STPs appear to support this observation. Other work by Petrasek et al.(10) indicated that primary sludges are likely to be sinks for metals and those organic compounds which have a propensity for adsorption. Unfortunately, no Niagara STP sludge samples were collected.

In 1984, a study of the removal of PAHs, metals and selected contaminants in the PCB/pesticide group was conducted at the Hamilton, Ontario STP(11). Metals were found to be present at concentrations ranging from 10 to 90 µg/L in the treated effluent, while PAHs were typically detected in the 0.1 to 0.8 µg/L range and PCB/pesticides in the 0.01 to 0.10 µg/L range.

TABLE 3 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN NIAGARA REGION STP EFFLUENTS(CITED BY 8).

CONTAMINANT (µg/L)	WELLAND		FORT ERIE		NIAGARA FALLS	
	Inf.	Eff. ¹	Inf.	Eff. ¹	Inf.	Eff. ¹
Volatiles						
Benzene	<0.1	L	0.2	2.1	<0.1	L
Chloroform ^{2 3}	1.3	2.4	9.9	11	9.7	4.6
1,2-Dichlorobenzene ³	1.7	L	4.1	5.2	0.6	3.1
Ethyl benzene	0.1	L	0.1	1.2	<0.1	L
Methylene chloride ^{2 3}	<5	8.1	53	L	88	5.2
Tetrachloroethylene ^{2 3}	0.2	L	6.4	12	4.3	1.6
Toluene ^{2, 3}	3.0	L	12	10	0.8	2.2
1,1,1-Trichloroethane ^{2 3}	0.1	L	4.8	4.3	0.2	1.3
o-Xylene	0.3	L	0.3	2.0	0.1	L
m-Xylene ³	0.4	L	5.0	3.7	0.1	L
Metals						
Chromium ²	20	5.0	8.0	6.0	6	L
Copper ²	54	67	30	20	50	33
Zinc ²	140	L	70	50	95	29
Inorganics						
Cyanide ²	0.2	L	1.0	7.0	40	16

¹ Mean values for those contaminants present in treated effluents at concentrations greater than 1.0 µg/L for more than 50% of the time. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

² In the list of the most frequently found effluent contaminants of both 25 and 40 POTW Studies.

³ In the list of the most frequently found effluent contaminants in the Metro Toronto STP Survey(8).

A very detailed survey of STP effluent trace contaminants is being conducted in an Environment Canada/Ontario Ministry of Environment (EC/MOE) assessment of the dynamic variability of trace contaminants in raw STP wastewaters and their treated effluents(12). One hundred grab samples of both streams were taken at two hour intervals over eight consecutive days at three Southern Ontario STPs in 1986. They were analyzed for volatile, metal and PAH contaminants. Mean values for those contaminants that were present in treated effluents with mean concentrations greater than 1.0 µg/L are presented in Table 4. These data should be regarded as preliminary in view of the fact that the study is still in progress.

All three STPs were secondary plants which produced good quality effluents as defined by effluent FOC and TSS. Some excess solids were discharged at Galt due to severe rainstorm conditions that occurred during part of the study. All three STPs show a significant presence of metal contaminants. Both Welland and Waterloo had minimal organic contaminants in their effluents which, in part, is corroborated by the Welland data collected earlier (Table 3). The Galt STP effluent contained low concentrations six organic contaminants. Three of these were in the list of the most commonly occurring effluent contaminants in both the 25 and 40 POTW Studies. PAHs were not found in the influents or the effluents at all three STPs.

A joint U.S.-Canadian Survey is underway of the major point source discharges to the waterways between the Great Lakes. Known as the Upper Great Lakes Inter-Connecting Channel Study (UGLCCS), the survey addressed the St. Clair River in 1985. Data have been extracted from this study which are specific to the STPs that were sampled at that time(13). Between three and seven composite samples were taken of influents and effluents on consecutive days in October, 1985. Those contaminants that occurred above 1 µg/L for more than 50% of the time in the final effluent are shown in Table 5. Data for these contaminants should be regarded as preliminary because the project is still in progress.

The Little River and Belle River STPs are secondary plants. A high quality nitrified effluent was produced at Little River and a partially

TABLE 4 CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE EC/MOE VARIABILITY STUDY EFFLUENTS(12)

CONTAMINANT (µg/L)	WATERLOO		WELLAND		GALT	
	Inf.	Eff. ¹	Inf.	Eff. ¹	Inf.	Eff. ¹
Volatiles						
Chloroform ²	5.2	1.0	5.1	L	3.3	1.0
1,4-Dichlorobenzene	2.9	L	2.2	L	4.2	1.4
Tetrachloroethylene ²	ND ³	ND	ND	ND	27.7	8.6
1,1,1-Trichloroethane ²	1.4	L	ND	ND	5.2	2.2
Trichloroethylene	1.7	L	1.3	L	4.4	1.0
p- & m-Xylene	50.4	L	1.2	L	39.6	1.0
Metals						
Cadmium	4.5	4.3	2.9	2.6	6.2	2.4
Chromium ²	54.2	29.8	16.5	9.3	92.8	31.0
Copper ²	122	14.3	34.1	6.3	146	49.2
Nickel ²	27.3	24.7	15.1	13.3	111	66.6
Lead	20.4	6.7	12.2	5.6	13.9	5.4
Zinc ²	152	81.4	76.2	22.9	199	83.2
Conventional (mg/L)						
FOC	48.0	13.2	28.0	8.2	51.0	16.5
TSS	137	5.8	73.9	3.8	102	34.2

¹ Mean values for those contaminants present in treated effluents with mean concentrations greater than 1.0 µg/L. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

² In the list of the most frequently found effluent contaminants of both 25 and 40 POTW Studies.

³ ND - Not detected.

TABLE 5 CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE UGLCCS STP EFFLUENTS(13)

CONTAMINANT (µg/L)	LITTLE RIVER		BELLE RIVER		WINDSOR WESTERLY	
	Inf.	Eff. ¹	Inf.	Eff. ¹	Inf.	Eff. ¹
Volatiles						
Bromodichloromethane	0.5	L	0.3	5.8	1.4	1.4
Chloroform ^{2 3}	5.0	17.6	4.6	7.3	6.0	6.4
Dibromochloromethane	ND ⁴	L	ND	2.3	ND	L
Ethyl benzene	0.2	ND	<0.1	ND	5.5	9.6
Methylene chloride ²	2.8	L	2.3	L	11.9	12.5
Tetrachloroethylene ^{2 3}	0.7	L	<0.1	L	36.4	69.0
1,1,1-Trichloroethane ^{2 3}	0.4	ND	ND	ND	2.5	2.0
Toluene ²	3.2	3.4	0.7	L	17.4	21.0
p- & m-Xylene ³	0.7	ND	0.2	L	83.5	40.4
o-Xylene	0.4	ND	0.1	L	11.4	17.0
Base Neutrals						
1,2-Dichlorobenzene	0.5	ND	1.7	L	1.5	1.9
1,4-Dichlorobenzene	1.5	L	1.0	L	1.8	1.5
Bis(2-EH)phthalate ²	17.3	5.3	10.7	79.3	25.3	12.8
Butyl benzyl phthalate	5.5	L	2.3	L	4.3	7.7
Di-n-butyl phthalate ²	55.0	47.8	11.3	16.7	58.3	22.0
Diethyl phthalate	13.0	L	10.6	L	8.2	4.8
Di-n-octyl phthalate	21.0	16.7	17.6	27.7	16.3	21.7
Metals						
Chromium ^{2 3}	32	8	20	L	56	10
Copper ^{2 3}	41	18	40	10	46	22
Nickel ²	19	10	20	L	39	37
Zinc ^{2 3}	196	73	50	36	329	125
Conventional (mg/L)						
BOD5	95	4	63	3	84	32
TSS	96	13	44	3	104	12
NH ₃ N	12	0.4	12	2.7	7	6

¹ Mean values for those contaminants present in treated effluents with mean concentrations greater than 1.0 µg/L. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

² In the list of the most commonly found effluent contaminants in both 25 and 40 POTW Studies.

³ In the list of the most frequently found effluent contaminants in both the Niagara Region and the EC/MOE Variability Studies.

⁴ ND - Not detected.

nitrified effluent at Belle River. Windsor Westerly STP is a primary plant that also produced a good quality effluent. As was observed in the comparison between the Niagara Region STPs (Table 3), there is a greater pass through of organic contaminants at the primary plant when compared to the secondary plants. The level of pass through appears to be greater at the Windsor Westerly STP than either Fort Erie or Niagara Falls STPs in terms of the volatile contaminants. All three STPs recorded the presence of phthalate esters which were not analyzed for in the Niagara Region Study. Of the seven organic contaminants listed in Table 5 for Little River and Belle River, four were in the list of the most frequently occurring contaminants in the 25 and 40 POTW Studies. For Windsor Westerly, however, seventeen organic contaminants are listed in Table 5 of which seven were in the 25 and 40 POTW list. Metal contaminants were prevalent in all three STP effluents similar to the observation at Niagara Region. There are inadequate data to demonstrate whether there is a significant difference in metals remaining in the effluent after primary versus secondary treatment.

U.S. Facilities

No large survey has been carried out in the U.S. since the completion of the 25 and 40 POTW Studies, probably as a result of the high cost. The literature shows that only some of the large U.S. municipalities have undertaken limited surveys of trace contaminant removal in STPs.

A one year investigation, called the Toxicant Pretreatment Planning Study (TPPS), was conducted by the Municipality of Metropolitan Seattle of Metro's two STPs(14). Seventeen 24 hr flow composited samples of influents and effluents were collected during the period 1980 to 1981. Those contaminants that occurred above 1 µg/L for more than 50% of the time in the final effluent are shown in Table 6. The Renton plant is a secondary plant which produced a high quality effluent during the Study as defined by the conventional parameters. Nine organic contaminants are listed in Table 6 of which five are from the 25 and 40 POTW list (Table 1). West Point is a primary plant and demonstrated a greater pass through of contaminants than Renton. Thirteen frequently occurring organic contaminants were identified; nine were the same as those at Renton and were

TABLE 6 - CONCENTRATION OF MOST FREQUENTLY FOUND TRACE CONTAMINANTS IN THE TIPS STP EFFLUENTS(14)

CONTAMINANT (µg/L)	RENTON		WEST POINT	
	Inf.	Eff. ¹	Inf.	Eff. ¹
Volatiles				
Benzene	2.6	2.8	3.1	3.8
Chloroform ²	2.9	2.8	9.1	7.4
Ethyl benzene	1.8	L	8.1	10.4
Methylene chloride ²	37.1	29.2	45.3	57.1
Tetrachloroethylene ²	20.0	3.9	14.7	18.7
Trichloroethylene	22.2	2.6	11.7	8.3
Toluene ²	9.5	L	47.0	51.2
Base Neutrals				
Naphthalene	ND ³	ND	12.7	10.4
Butyl benzyl phthalate	56.8	19.0	57.3	48.5
Diethyl phthalate	8.9	1.7	4.2	5.3
Di-n-butyl phthalate ²	48.6	32.8	40.3	38.8
Di-octyl phthalate	49.2	10.8	21.7	60.1
Acid Extractables				
Phenol	67.6	L	46.7	42.5
Metals				
Antimony	1.4	2	5.5	7
Arsenic	4.9	2	3.8	4
Cadmium	7.8	1	7.2	4
Chromium ²	86	33	120	64
Copper ²	200	29	180	88
Lead	120	25	160	74
Nickel ²	57	31	64	51
Silver	13	3	13	8
Zinc ²	240	64	340	140
Inorganics				
Cyanide ²	26	27	47	59
Conventionals (mg/L)				
BOD5	242	20	207	132
TSS	211	20	215	104

¹ Mean values for those contaminants present in treated effluents with mean concentrations greater than 1.0 µg/L. Other values designated L indicate that the contaminant occurred less than 50% of the time. Corresponding influent concentrations are mean values.

² In the list of most frequently found effluent contaminants in both 25- and 40 POTW Studies.

³ ND - Not detected.

present at higher concentrations. Nine metal contaminants were identified as occurring frequently at both plants; four were on the 25 and 40 POTW lists.

The Ohio and Wisconsin State Environmental Protection Agencies and the Metropolitan Sanitary District of Greater Chicago (MSDGC), have conducted limited organic analysis of STP effluents during the period 1983 to 1984 (cited by 8). The most frequently found contaminants were very similar at all locations. Common to the surveys were the following six contaminants:

<u>Volatiles</u>	<u>Base Neutrals</u>
Chloroform	Bis(2-EH)phthalate
Methylene chloride	Di-n-octyl phthalate
1,1,1-Trichloroethane	
Trichloroethylene	

Four of these were on the list of most frequently found contaminants in the 25- and 40 POTW Studies (Table 1). The Wisconsin EPA (WEPA) and the MSDGC listed six additional frequently occurring contaminants:

<u>Volatiles</u>	<u>Base Neutrals</u>
Benzene (WEPA only)	1,4-Dichlorobenzene (WEPA only)
Tetrachloroethylene	Diethyl phthalate
Toluene (WEPA only)	Di-n-butyl phthalate (WEPA only)

These contaminants were also frequently found in the studies cited above.

Discussion of Survey Results

Trace contaminant data were screened from 105 municipal treatment plant effluents in Canada and the U.S.. The period over which these data were collected ranged from 1978 to 1986. The contaminants listed below were found most frequently in STP effluents. Cyanide was also found when tested for.

Volatiles

Chloroform
Methylene chloride
Tetrachloroethylene
Toluene
1,1,1-Trichloroethane
p- & m-Xylene

Phthalates

Bis(2-ethyl hexyl)phthalate
Di-n-butyl phthalate
Diethyl phthalate

Metals

Cadmium
Chromium
Copper
Lead
Nickel
Zinc

The chlorinated solvent compounds, chloroform, methylene chloride, tetrachloroethylene and trichloroethane were found most frequently, and, to a lesser extent, the solvents toluene, ethyl benzene and the chlorinated benzenes were also found. More recent surveys have identified the frequent presence of xylenes. In well operated secondary plants, the level of the most commonly found volatiles ranged from 1 to 20 $\mu\text{g/L}$. For methylene chloride and other chlorinated compounds the higher effluent values may be distorted. Methylene chloride is used as the extracting solvent in the analytical protocol for USEPA priority pollutants. It can occur as a contaminant in laboratory glassware. Also, chlorination of treated effluents can increase the level of purgeable organics in final effluents over that found in raw wastewaters. Where chlorination does not occur, purgeable compounds are usually removed to a high degree but may still be present above detectable levels. In primary STPs, the same types of purgeable compounds were observed. Their concentration may be higher than in secondary STP effluents.

Not all effluents were measured for phthalates. However when this was carried out, all effluent samples contained phthalate esters. Their widespread use in plasticizers leads to their ubiquitous presence in all wastewater samples. They are among the most commonly occurring organic contaminants in treated effluents. Metal contaminants occurred at greater concentrations than the organic contaminants, ranging from 1 to 100 µg/L in secondary effluents and often higher in primary effluents.

The absence of phenolic compounds in treated effluents may be attributed to biological oxidation. However, this may not be appropriate for primary plants. The method of measuring phenol is not frequently reported. The extraction efficiency of phenol by methylene chloride can be low depending upon organic matrix effects. Therefore, artificially low values can be reported. This phenomenon may be avoided by measuring phenol by the 4-amino antipyrine method.

The effectiveness of secondary treatment plants can be demonstrated by comparing influent and effluent data. In many cases, contaminants occur less than 50% of the time in treated effluents despite their relatively high influent values.

There has been concern over the presence of PAHs in effluent discharges. The EC/MOE Variability Study measured 100 samples of influent and effluent at two hour intervals over eight days at three different STPs. Despite this rigorous investigation, PAHs were rarely, if ever, detected in either influents or effluents.

In summary, well operated secondary STPs can produce high quality effluents that contain small numbers of frequently occurring priority pollutants. Typically, between five and ten organic contaminants were found at concentrations ranging from 1 to 20 µg/L more than 50% of the time. The significance of the ubiquitous presence of methylene chloride and the phthalate esters in all effluent samples is not understood at this time. In addition, between three and six metal contaminants were found more than 50% of the time at concentrations ranging from 1 to 100 µg/L.

TECHNOLOGY OF CONTAMINANT REMOVAL

It may be possible to further improve the effluent quality that is being achieved at the present time by a better understanding of contaminant removal mechanisms. A review of the current knowledge on removal mechanisms follows.

In parallel with STP performance assessments, considerable work has been carried out since 1978 to improve the understanding regarding toxic contaminant removal in wastewater treatment plants. Most work has addressed the activated sludge system with very little work directed to primary or other secondary plants. What has emerged is the knowledge that the mechanism(s) of removal are complex and do not lend themselves readily to predictive models. It has been established that organic contaminants can be removed in secondary plants by adsorption, volatilization and by biological oxidation. Metal contaminants may be removed by either precipitation or adsorption. If removal does not occur by one of these mechanisms, the contaminants pass through to the final effluent and are discharged.

Several attempts(15,16,17) have been made to mathematically model the contaminant removal mechanisms. Of these attempts, the volatilization and biosorption models are better developed than the biodegradation model. It is likely that a limited number of microbial species may be responsible for biodegradation of a specific contaminant. However, since isolation of the microorganisms or enzymes is almost impossible, no adequate mechanistic model has been developed. The predictive equations are derived from steady-state conditions which are not representative of the typical operation of an STP. The existing models cannot address dynamic behaviour. They have not been field tested because of this drawback.

Early work by the USEPA assessed the removal of trace contaminants in well operated and acclimated pilot-scale activated sludge systems(10,18,19). Process performance was evaluated using controlled influent concentrations of priority pollutants in municipal wastewaters. Typical spiked concentrations of the contaminants ranged from 50 to 200 µg/L. More than 95% removal of acid extractable and base neutral contaminants was achieved, with more than 98%

removal for the volatiles. Trace metal removals were lower, ranging from 20 to 90%. An important observation was, that at the levels of contaminant tested, inhibitory or interference effects were not observed on the biological treatment system when operated at steady-state.

Treatability investigations sponsored by the USEPA(16,20) suggested that the abiotic removal mechanisms could dominate biological oxidation. Contaminants could partition to sludges which could prevent land disposal of such sludges. Alternatively, they could volatilize into the air from sewers, headworks and aeration basins. The contribution of the three mechanisms to removal has been estimated by many researchers. Unfortunately, removal has not always been attributed to the correct mechanism(8). Consequently, direct comparison of removals attributed to specific mechanisms is not always possible.

The experimental work of Weber and Jones(16), Kirsch et al.(20), Kincannon et al.(21) and Lawson and Siegrist(22) indicated that volatilization and biodegradation were the major removal mechanisms, with adsorption being less important. The USEPA addressed the relative importance of the removal mechanisms through non-experimental procedures(23). In this procedure, the USEPA first established the removal of a compound and then estimated the proportion of the contaminant removed by volatilization based on USEPA data. The proportion of the compound that was adsorbed to the biomass was estimated from the 40 POTW Study data(1) while the proportion biodegraded was calculated by the difference. The procedure is useful in that it differentiates between acclimated and unacclimated systems. The procedure indicated that volatile contaminants are removed primarily by volatilization, or biodegradation, depending upon the degree of acclimation of the activated sludge. Volatilization may be the dominant mechanism when the activated sludge system is not acclimated. Conversely, if the biomass is acclimated, biodegradation may be the important mechanism. This effect has been demonstrated by Bedford and Melcer(24) for trichloroethylene. In the base neutral group, the chlorinated benzenes are removed by volatilization and biodegradation. With the non-experimental approach, adsorption was assigned a greater role than in previous studies. The phthalate esters were predicted to be removed by a combination of biodegradation and adsorption. PAHs appear to be degraded and adsorbed. Phenolic compounds appear to be biodegraded primarily.

CONTROL TECHNOLOGY

Trace contaminants may be removed by volatilization, adsorption or biological oxidation. In view of the potential problems associated with the loss of contaminants by the first two mechanisms, a reduction in effluent emissions could best benefit from an improvement in the biological oxidation mechanism. Substrate inhibition and microbial growth rate are important process considerations in the biological degradation of trace contaminants. To minimize substrate inhibition, measures could be taken to reduce the influent contaminant concentration by minimizing the input of the contaminants to the sewer. This is a matter which is beyond the scope of this paper.

Microorganisms that can degrade complex organic contaminants have low growth rates. The inverse relationship between the specific microbial growth rate and SRT permits the control of growth rate through SRT manipulation. To prevent the washout of slow-growing microorganisms, a minimum SRT must be maintained such that microbial growth can proceed at, or less than, its maximum rate. Wash-out will then be prevented. To minimize construction costs, it is desirable that HRT and SRT be adjustable independently. In fixed film systems, such as rotating disc contactors and biological fluidized beds, this can be achieved readily. In activated sludge systems, SRT may be manipulated by adjustment of sludge recycle rate and sludge wasting.

Several researchers (25-28) have demonstrated the importance of SRT manipulation for removal of trace contaminants in activated sludge systems. The latter two studies showed that a minimum SRT of five days was required for the removal of 4,6-dinitro-o-cresol from municipal sewage and ten days for the removal of pentachlorophenol, also from municipal sewage. Lower SRTs resulted in pass through of the contaminant and a deterioration in settling performance.

CONCLUSIONS

- A survey of treated effluents from 105 municipal wastewater treatment plants indicated that very low levels of USEPA priority pollutants can be

achieved in the effluents from well operated secondary plants despite the often high levels that occurred in raw wastewaters. A greater pass through of both organic and inorganic contaminants occurred in primary plants.

- The most commonly occurring contaminants from the volatile, acid extractable, base-neutral and metal groups of the priority pollutants, were the volatile chlorinated compounds, phthalate esters and metals. PAHs were not frequently found.
- Typically, for well operated secondary STPs, between five and ten organic contaminants were found at concentrations ranging from 1 to 20 µg/L more than 50% of the time in the effluents. Between three and six metal contaminants were found more than 50% of the time, ranging in concentrations from 1 to 100 µg/L.
- Trace contaminants are removed in municipal wastewater treatment systems via volatilization, adsorption and biodegradation mechanisms. The contribution made by each mechanism for a specific contaminant is not well known or understood. Modelling of the removal mechanisms is at an early stage.
- The concept of SRT manipulation has been demonstrated to achieve control of trace contaminants in municipal activated sludge systems.

REFERENCES

1. Burns and Roe Industrial Services Corporation, "Fate of Priority Toxic Pollutants in Publicly Owned Treatment Works - Final Report", Vol.1, EPA-440/1-82/303, 1982.
2. Hannah, S.A. and L.A. Rossman, "Monitoring and Analysis of Hazardous Organics in Municipal Wastewater - A Study of 25 Treatment Plants". NTIS Pub.No. PB83-155713, 1982.
3. Bonner, R.F. and O. Meresz, "St. Clair River Organics Study - Identification and Quantitation of Organic Compounds". Ontario Ministry of Environment, Toronto, Ont., 1981.

4. Water Pollution Control Directorate, "Draft Summary Report: Toxic Screening Studies at Municipal Sewage Treatment Plants 1979-1981". Abatement and Compliance Branch, Municipal Division, Environment Canada, Ottawa, Ont., 1982.
5. Rossman, L.A. and J.J. Convery, "A Perspective on Performance Variability in Municipal Wastewater Treatment Facilities", NTIS Pub.No. PB86-176377, 1986.
6. Bridle, T.R. et al., "Biological Treatment of Coke Plant Wastewaters For Control of Nitrogen and Trace Organics". Presented at the 53rd Annual Water Pollution Control Federation Conference, Las Vegas, 1980.
7. Mann Testing Laboratories, "Trace Organic Analysis of WPC Plant Influent and Effluent". Report to the Municipality of Metropolitan Toronto, Metro Works Department, Toronto, Ont., 1986.
8. Canviro Consultants Ltd., "A Novel Application of a Time Series Modelling Approach to the Management of Dynamic Fluctuations in Trace Contaminants in Sewage Treatment Plants" - Phase 1 Report: Technical Review. Wastewater Technology Centre, Environment Canada, Burlington, Ont., 1986.
9. Hannah, S.A., et al., "Comparative Removal of Toxic Pollutants by Six Wastewater Treatment Processes", J.Wat. Pollut. Contr. Fed., 58(1), 27, 1986.
10. Petrasek, A.C. and I.J. Kugelman, "Metals Removals and Partitioning in Conventional Wastewater Treatment Plants", J. Wat. Pollut. Contr. Fed., 55(9), 1183, 1983.
11. Canviro Consultants Ltd., "Removal of Hazardous Contaminants in the Hamilton WPCP". Draft Report submitted to Ontario Ministry of Environment, Toronto, Ont., 1984.
12. Canviro Consultants Ltd. Preliminary Data from the Study on the Management of Dynamic Fluctuations in Trace Contaminants in Sewage Treatment Plants. Wastewater Technology Centre, Environment Canada, Burlington, Ont., 1986.
13. Environment Canada. Preliminary Data from Great Lakes Inter-Connecting Channel Study. Toronto, Ont., 1986.
14. Cooley, R. and R. Matasci, "Toxicant Pretreatment Study Technical Report A1-Treatment Plant Evaluation". Report to Municipality of Metropolitan Seattle, WPC Department., Seattle, WA., 1984.
15. Blackburn, J.W. et al., "Organic Chemical Fate Prediction in Activated Sludge Treatment Processes". NTIS Report No. PB85-247674, 1985.
16. Weber, W.J. and B.E. Jones, "Toxic Substance Removal in Activated Sludge and PAC Treatment Systems". NTIS Report No PB86-182425, 1986.
17. Moos, L.P. et al., "Pentachlorophenol Biodegradation - I (Aerobic)", Wat. Res., 17, 1575, 1983.
18. Petrasek, A.C. et al., "Fate of Toxic Organic Compounds in Wastewater Treatment Plants", J. Wat. Pollut. Contr. Fed., 55(10), 1286, 1983.
19. Petrasek, A.C. et al., "Removal and Partitioning of Volatile Organic Priority Pollutants in Wastewater Treatment Plants". Proc. of 9th U.S.-Japan Conf. on Sewage Treatment Technology, EPA-600/9-85/014, 1985.
20. Kirsch, E.J. et al., "Fate of Eight Organic Priority Pollutants", Draft Report, EPA Cooperative Agreement No. CR-807630-10, WERL, USEPA, Cincinnati, 1986.
21. Kincannon, D.F. et al., "Removal Mechanisms for Toxic Priority Pollutants", J. Wat. Pollut. Contr. Fed., 55, 157, 1983.
22. Lawson, C.T. and S.A. Siegrist, "Removal Mechanisms for Selected Priority Pollutants in Activated Sludge Systems", Proc. of ASCE Nat. Conf. on Environ. Eng., 356, 1981.
23. U.S. Environmental Protection Agency, "Report to Congress on the Discharge of Hazardous Wastes to Publicly Owned Treatment Works. EPA/530-SW-86-004, 1986.
24. Bedford, W.K. and H. Melcer, "Fate of Trichloroethylene in Activated Sludge Systems". Presented at 21st Canadian Symposium on Water Pollution Research, Burlington, Ontario, 1986.
25. Wukasch, R.P. et al., "Prediction of the Fate of Organic Compounds in Biological Wastewater Treatment Systems". AIChE Symposium Series (Water 1980), No. 209, 137, 1981.
26. Bridle, T.R. et al., "Biological Nitrogen Control of Coke Plant Wastewaters", Wat.Sci.Tech., 13(1), 667, 1981.
27. Melcer, H. and W.K. Bedford, "The Fate of 4,6-Dinitro-o-cresol in Municipal Activated Sludge Systems". Presented at the International Conference on Innovative Biological Treatment of Toxic Wastewaters, Arlington, VA, 1986.
28. Melcer, H. and W.K. Bedford, "Removal of Pentachlorophenol in Municipal Activated Sludge Systems". Presented at the 59th Annual Water Pollution Control Federation Conference, Los Angeles, 1986.

DESIGN OF PILOT PROGRAM FOR ORGANICS REMOVAL AT NIAGARA FALLS

J.N. Hilton*, R.F. Machacek*, M.C. Kavanaugh** and K.J. Roberts***

*MacLaren Plansearch Inc., 33 Yonge Street, Toronto, Ontario, Canada M5E 1E7

**James M. Montgomery, Consulting Engineers Inc., 250 N. Madison Avenue,
Pasadena, California, U.S.A. 91109

***Ontario Ministry of the Environment, 1 St. Clair Ave. West,
Toronto, Ontario, Canada M4V 1K6

ABSTRACT

As public concern for the quality of drinking water in Ontario continues to grow, considerable research has been undertaken to re-examine conventional treatment methodologies as well as alternate processes for the removal of trace levels of organic chemicals, including adsorption by granular activated carbon (GAC).

This project has been undertaken to determine the following:

- the effectiveness of optimized conventional drinking water treatment for the removal of trace organic contaminants
- the effectiveness of activated carbon adsorption removals of trace organic contaminants when used in the add-on contactor mode
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal.

Jar testing and pilot plant operations will be conducted on site at the Niagara Falls Water Treatment Plant, using the Niagara River as the raw water source.

This paper summarizes work performed thus far on the selection of target monitoring compounds, the development of analytical protocols, the proposed experimental plan (including jar testing, conventional treatment, GAC treatment), the design of the pilot plant, and the analysis of data.

KEYWORDS

Trace organics removal; drinking water treatment; adsorption; granular activated carbon; homogeneous surface diffusion model; equilibrium column model.

INTRODUCTION

Public concern for the quality of drinking water in Ontario continues to grow, as advances in analytical capabilities result in the detection of an increasing number of synthetic organic compounds (SOC) in raw waters. This awareness has been

heightened by widespread publicity from the news media of the presence of even the smallest concentrations of organics in raw and finished drinking water supplies.

As a result, considerable research is being undertaken to re-examine conventional treatment methodologies as well as alternate processes for the removal of trace levels of organic chemicals, including adsorption by granular activated carbon (GAC).

This project has been undertaken to determine the following:

- the effectiveness of optimized conventional drinking water treatment for the removal of trace organic contaminants
- the effectiveness of activated carbon adsorption removals of trace organic contaminants when used in the add-on contactor mode
- process operational parameters for the optimized operation of full scale water treatment plants and GAC adsorbers used in the add-on mode for organics removal.

The project comprises three components. The first component includes a review of existing data on ambient water quality, development of analytical and sampling protocols, experimental design development and the physical design and set-up of the pilot plant equipment. Component II consists of organic removal studies at Niagara Falls, Ontario, including jar testing and pilot plant operation. Jar testing will determine an initial choice of coagulant for conventional treatment and will be re-evaluated throughout the year. The pilot plant will model a complete water treatment process and will operate to optimize organics removal conventional processes for a period of two weeks. The pilot plant will then operate with GAC fixed beds in the add-on contactor mode for a period of 52 weeks. The third component consists of data evaluation including results of GAC modelling runs. The ultimate goal is to generate data that will be of a nature to develop pertinent design criteria and serve as a technical basis for policy regarding drinking water quality and required treatment in Ontario.

At this time, work on Component I is nearing completion. This paper summarizes work performed thus far on the selection of target monitoring compounds, the development of analytical protocols, the proposed experimental plan (including jar testing, conventional treatment, GAC treatment), the design of the pilot plant, and the analysis of data.

SELECTION OF TARGET COMPOUNDS

The initial selection process for target compounds to be monitored during the pilot plant operation began with a list of over 300 organic chemicals that have been found in the Great Lakes ecosystem. This list was compiled from several different references, including work by the International Joint Commission (IJC, 1983), the Niagara River Toxics Committee (NRTC, 1984), the Ontario Ministry of the Environment (MOE, 1984, 1985a, 1985b), the New York Public Interest Group (NYPIRG, 1981), the City of Toronto Department of Public Health (City of Toronto, 1984) and the Municipality of Metropolitan Toronto Department of Works (Municipality of Metro Toronto, 1983).

The following information was gathered for each chemical:

Identification

Chemical Name

CAS - Chemical Abstracts Service Registry Number

Environmental Levels

The frequency and maximum amount detected in the Niagara Falls water treatment plant raw water by routine, bi-weekly MOE monitoring of organics.

Physical, Chemical and Toxicological Properties

Henry's Law Constant
Aqueous Solubility
log Kow
Complexation Potential with TOC
Liquid Phase Diffusion Coefficient
Activated Carbon Capacity
Bioconcentration Factor
LC50
LD50
NRTC Hazard Class Rating

Aquatic and Drinking Water Criteria

Ministry of the Environment
U.S. Environmental Protection Agency
World Health Organization

The initial screen of all the chemicals found in the Great Lakes ecosystem was based on the availability of quantitative environmental and toxicological data. Compounds without much data available were given little further consideration. The second screen for chemicals with quantitative data was based mainly on the Categories of Concern developed by the Niagara River Toxics Committee (NRTC, 1984). One of the principal tasks of the NRTC was to assess the significance of the types and levels of chemicals found in the Niagara River. The screening methodology involved in establishing a priority ranking involved three major types of information. Criteria information was taken from several agencies and included criteria for the protection of aquatic life, human health, etc. Chemical and toxicological information included bioaccumulation and acute toxicity data, and other health parameters considered in various other toxicity scoring methodologies. Environmental occurrence information was compiled from responsible jurisdictions involved in the Niagara River Toxics Project. The screening process resulted in three major groups and several subgroups of chemicals, of which group I, and groups IIA and IIB chemicals are considered to be of most concern. This is based on concentrations of these chemicals identified in the Niagara River with respect to levels at which they are considered to pose risks to human health and/or environment. Designation as an EPA priority pollutant was also considered in the screening process.

For this project, chemicals listed as NRTC group I, IIA or IIB compounds or as EPA priority pollutants were screened again to determine if they were present in the raw water supply at the Niagara Falls Water Treatment Plant. This was accomplished by reviewing MOE routine, biweekly monitoring of several classes of organic compounds in the Niagara raw water over a period of two years. This was done to help establish sampling and spiking needs in the overall experimental plan.

Compounds not passing previous screens were then considered against other com-

pounds in the same chemical class (e.g. pesticides, phthalates, polyaromatic hydrocarbons). An attempt was made to have a complete range of high to low values of chemical and physical properties that affect organic chemical removal processes represented within each chemical class. For example, Henry's Law Constants provide an indication of the ability of a chemical to be removed by aeration or air stripping processes. Compounds that were felt to contribute to the overall range of properties within their class were considered further.

The final acceptance criteria was based on practical considerations for the spiking, sampling and analytical programs. Chemicals that presented problems were rejected. For example, compounds for which acceptability low detection limits could not be achieved were excluded. Another example is the phthalates (i.e. bis(2-ethylhexyl) phthalate and di-n-butylphthalate) which are ubiquitous as laboratory contaminants.

The total number of target compounds is limited by budget constraints, as analytical costs for regular monitoring of 34 organic compounds are quite large. The list of target compounds chosen is shown in Table 1.

TABLE 1 List of Target Compounds

<u>Chemical Class</u>	<u>Compounds</u>
Halogenated Aliphatics	Chloroform Carbon tetrachloride 1,2-dichloroethane Hexachlorobutadiene Tetrachloroethylene
Aromatics	Benzene o-Xylene Nitrobenzene
Chlorinated Benzenes	Chlorobenzene 1,4-dichlorobenzene Hexachlorobenzene 1,2,4-trichlorobenzene
Chlorinated Phenols	2,4,6-trichlorophenol Pentachlorophenol
PCB's	2,5,2'-trichlorobiphenyl 2,5,2',5'-tetrachlorobiphenyl 2,4,5,2',5'-pentachlorobiphenyl 2,4,5,2',4',5'-hexachlorobiphenyl 2,3,4,5,2',3',4',5'-octachlorobiphenyl
Organochlorine Pesticides	p,p'-DDT Heptachlor epoxide beta-BHC
Chlorophenoxy Herbicides	2,4-D
PAH's and Related Compounds	Anthracene Benzo(a)pyrene Naphthalene Pyrene

Phthalates	Di-n-octylphthalate
Alcohols and Esters	1-decanol Isobutanol Methyl hexadecanoate
Alkanes	Decane Hexadecane Hexane

ANALYTICAL PROTOCOL DEVELOPMENT

The 34 compounds selected for this project have been divided into five analytical fractions based on their chemical properties. These five analytical fractions and the compounds belonging in each category are summarized below.

High Volume Volatile Organic Analysis

An optimization of the classic purge-and-trap analysis wherein 100 mLs of water are purged with helium onto an adsorbent trap and desorbed into a capillary column with GCMS detection.

chloroform
carbon tetrachloride
1,2-dichloroethane
tetrachloroethane
benzene
xylene
chlorobenzene
1,4-dichlorobenzene
1,2,4-trichlorobenzene
isobutanol
hexane
decane
naphthalene

High Volume Base/Neutral Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is extracted serially with methylene chloride at high pH and the final extract analysed by GCMS.

nitrobenzene
di-n-octylphthalate
1-decanol
methyl
hexadecanoate
hexadecane

High Volume Organochlorine Pesticides Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is extracted serially with methylene chloride, the solvent switched to hexane and the final extract analysed by GC/ECD.

hexachlorobenzene
hexachlorobutadiene
beta-BHC
p,p'-DDT
heptachlor epoxide
2,5,2'-trichlorobiphenyl
2,5,2',5'-tetrachlorobiphenyl
2,4,5,2',5'-pentachlorobiphenyl
2,4,5,2',4',5'-hexachlorobiphenyl
2,3,4,5,2',3',4',5'-octachlorobiphenyl

High Volume Polyaromatic Hydrocarbons Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is extracted serially with methylene chloride, the solvent switched to acetonitrile and the final extract analysed by HPLC with UV and fluorescence detectors.

anthracene
benzo (a) pyrene
pyrene
naphthalene

High Volume Chlorinated Phenol/Chlorophenoxy Herbicide Analysis

A modification of the liquid-liquid extraction procedure wherein a 16 liter sample is adjusted to low pH and serially extracted with methylene chloride, the solvent transferred to toluene, derivitized with a boron trifluoride reagent, and analysed by GC/ECD.

2,4,6-trichlorophenol
pentachlorophenol
2,4-D

Precision and Accuracy

Detection limits for the analytical methods used in this project have not yet been finalized. The method detection limit (MDL) will be used in the reporting of all results from organics analysis.

The MDL measures the minimum concentration of analyte required to yield a signal which is distinguishable from the signal due to the blank, and is generally much higher than the more typically reported instrument detection limit, which is based on a simple signal to noise response. The MDL is actually a function of method precision at low concentration levels, since the ability to distinguish a true signal from the blank is dependent on the variability of a replicate measurements for the blank and for low level samples. The MDL is, therefore, dependent on the standard deviation of replicate blank and low level sample replicates.

The MDL is based on hypothesis testing using the student's t statistic on the population of data obtained by replicate testing. The statistical values for a 99% confidence level have been applied to work on this project. The estimated MDL is calculated by multiplying the t statistic for 99% confidence and the appropriate degrees of freedom (dependent on number of replicates) by the standard deviation value measured for the replicates. Precision is reported as the rela-

tive standard deviation of replicate measurements of samples spiked with a known concentration of analyte. Accuracy is reported as the percent recovery of the mean of replicate measurements of samples spiked with a known concentration of analyte.

EXPERIMENTAL PLAN

Jar Testing Studies

The goal of the jar testing studies is to determine the optimum coagulant dose and operating pH for removal of turbidity and natural organic carbon. As a measure of natural organic carbon, dissolved organic carbon (DOC) and UV absorbance will be used. The optimum conditions will be selected through bench-scale testing at the beginning of pilot plant operation, and quarterly thereafter to adjust for seasonal water quality variations.

The jar tests will be used to screen a large number of potential coagulants, coagulant doses, and operating pH combinations. In general, optimum turbidity removal occurs at a higher pH than optimum DOC removal at a given coagulant dose. Thus, selection of a coagulant dose/pH combination represents a compromise between turbidity removal and DOC removal. Three factors must be integrated to determine the optimum dose: removal efficiency, sludge production and cost.

The coagulation optimization consists of a series of steps to evaluate a large number of options. The first step is to characterize the water quality with respect to the level of natural organics, turbidity, pH, alkalinity and buffer capacity. Step 2 is to evaluate the following primary coagulants: alum, polyaluminum chloride, ferric chloride, and CatFloc with alum (at a fixed alum dose). These tests will be done at a fixed pH. Following coagulation selection, step 3 tests would investigate the dose/pH relationship. The treated water quality will be used to generate DOC and turbidity isopleths as a function of pH and coagulant dose. The minimum coagulant dose giving DOC and turbidity removals will be compared, based on estimated costs of chemical addition and sludge disposal. Sludge production will be estimated from stoichiometry. The objective of step 4 is to determine the benefits of anionic, nonionic and long-chain cationic polymers as well as activated silica as secondary coagulants for improving DOC and/or turbidity removals.

Monthly average raw water turbidity at Niagara Falls varies from approximately 0.6 to 14 NTU throughout the year. Thus, the coagulant dose will also vary. Quarterly (or more frequent) jar test series will thus be conducted to determine coagulant dose, pH and polymer dose with changing raw water quality.

Evaluation of Organics Removal by Conventional Treatment

Goal. The goal of this phase of the study is to determine the effectiveness of conventional water treatment unit processes (e.g. coagulation, flocculation, sedimentation and filtration) in removing the target compounds.

Compound selection. Based on the selection of the 34 target compounds from among eleven groups of SOCs, fourteen "monitor" compounds were selected for this phase of the study. These compounds were selected to represent a wide range of physiochemical characteristics relevant to water treatment processes. These monitor compounds are:

- 1,2-Dichloroethane
- Tetrachloroethylene
- Benzene
- Chlorobenzene
- 1,4-Dichlorobenzene
- 2,4,6-Trichlorophenol
- PCB congeners
- p,p'-DDT
- beta-BHC (alpha-BHC)
- Anthracene
- Benza (a) pyrene
- Naphthalene
- Hexane

The Phase I monitor compounds span a molecular weight range of approximately 75 and 350. Available data are also plotted for the log₁₀ of the octanol:water partition coefficient, the log₁₀ of the Henry's constant, and the GAC capacity at exhaustion for an assumed influent concentration of 100 ug/L. The octanol:water partition indicates the hydrophobic nature of a compound, and the more hydrophobic compounds will tend to associate with particulate organic matter and could be removed through coagulation and sedimentation. A roughly inverse relationship exists between octanol:water partition coefficient and the Henry's constant, a measure of volatility. Thus, while some compounds are less hydrophobic, and not likely to be removed through settling of natural organic particulates, they may be removed through aeration.

Pilot plant operation. Once steady-state pilot plant operation is achieved, a spiking solution containing the fourteen monitor compounds will be made up in methanol and fed at a spiking port upstream of the coagulation/flocculation basin, resulting in a diluted concentration of approximately 10 ug/L. At this influent concentration and the expected detection limits of the analytical procedures to be used, removals of approximately 99 percent can be quantified. Samples will be taken for analysis of the raw influent, the spiked influent and the filter effluent.

Evaluation of Organics Removal by Fixed Bed GAC Adsorber

Goal. There are two goals for the second phase of this study. The first is to determine the effectiveness of GAC in removing ambient levels of SOC's from conventionally treated drinking water. The second is to obtain sufficient information to be able to predict the performance of fixed bed GAC contractors, under various scenarios of influent concentrations of SOC's. This requires calibration of the proposed model of multicomponent GAC adsorption.

Compound selection. A similar approach to that described above was taken for selecting Phase II monitor compounds from among the 34 target compounds. Compared to Phase I, however, a smaller number of compounds will be used because the computer can simulate the removal of up to six compounds only. The Phase II monitor compounds chosen are:

- Tetrachloroethene
- Benzene
- 1,2-Dichloroethane
- 1,4-Dichlorobenzene
- alpha-BHC
- Naphthalene

These compounds were chosen to represent a range of physicochemical properties. Because the goal of Phase II operation is to obtain GAC adsorption data, the six compounds were chosen to represent those compounds which may breakthrough a GAC adsorber at least within the time frame of the test period (i.e. 52 weeks).

Pilot plant operation. GAC is very effective in removing a number of the Phase II

monitor compounds following conventional treatment. For this reason, the pilot plant will be operated for 1 year in order to observe the breakthrough of strongly adsorbed compounds through the spiked columns.

Since the use of an organic solvent such as methanol would compete with the monitor compounds in the adsorption process, it is proposed that filtered water from the pilot plant be used as the spiking solution solvent. The spiking solution will be pumped from "no-headspace" containers to minimize volatilization of the compounds with higher Henry's constants. The spiking solution flow will be to the port upstream of the two spiking columns. The exact spiking protocol will be determined in the field because of the problems identified with preparation of aqueous spiking solutions.

Because of the high adsorption capacity of GAC for trace levels of the six monitor compounds, GAC column influent concentrations of 1000 ug/L were desired in order to observe breakthrough. Based on the solubilities reported, this column influent concentration can be achieved for four of the six compounds. Concentrations of only 276 ug/L and 558 ug/L can be achieved for alpha-BHC and naphthalene, respectively, because of their low aqueous solubilities. (Note: all calculations using alpha-BHC have been included in this discussion, as beta-BHC has only very recently been selected as a target monitoring compound to replace alpha-BHC.)

Sampling and analysis. To refine the sampling schedule preliminary GAC adsorption modelling runs were made for the pilot plant operating conditions by Dr. John Crittenden's group at Michigan Technological University.

Detailed discussion of the homogeneous surface diffusion model (HSDM), the equilibrium column model (ECM) and the ideal adsorbed solution theory (IAST) can be found elsewhere (Crittenden, 1985). A brief summary is given here.

The HSDM describes the fate of an adsorbate within a fixed-bed adsorber. It incorporates the mechanisms of advective flow, liquid-phase mass transfer resistance, local adsorption equilibrium at the exterior surface of the adsorbent, surface diffusion, and competitive equilibrium of solutes upon the carbon surface. The ECM divides the fixed bed into zones of constant composition that expand and move down the bed as solute accumulates on the adsorbent. The ECM defines the elution order of adsorbates, the highest overshoot concentration, the number of bed volumes that may be treated before the highest overshoot may occur, and the lowest GAC usage rate. Results from the ECM closely approximate actual breakthrough data for long columns, such as the 20 minute overall EBCT studied here.

Successful model predictions are dependent on good descriptions of multicomponent equilibria and mass transfer rates. The competitive equilibrium adsorption effects of multi-solute systems is estimated using IAST. This approach corrects the single solute isotherm for the competitive effects of other compounds in solution, since the presence of a more strongly adsorbing compound can reduce the degree of adsorption of a weaker adsorbing compound. The mass transfer parameters of film transfer coefficient, the surface diffusion coefficient, and pore diffusion coefficient describe the mass transfer rate and can be determined by thermodynamic correlations. The Freundlich capacity parameter and the Freundlich intensity parameter must also be determined for each adsorbing species.

Using the modified isotherms as determined by IAST for the six monitor compounds, the bed volumes treated until breakthrough can be estimated using ECM. Multiplying the bed volumes treated by the EBCT yields the time to breakthrough. The results of these calculations are listed in Table 2 for influent concentrations of 10, 100 and 1000 ug/L and EBCTs of 1, 10 and 20 minutes. The six monitor compounds are predicted to breakthrough in the order 1,2-dichloroethane,

1,4-dichlorobenzene, benzene, naphthalene, tetrachloroethane and alpha-BHC. The results illustrate the importance of using column influent concentrations of close to 1000 ug/L to observe breakthrough for at least a 10 minute EBCT within the year period for all compounds.

TABLE 2 Equilibrium Predictions of Breakthrough Times

	Empty Bed Contact Time (EBCT)		
	1 min	10 min	20 min
<u>alpha-BHC</u>			
1000 ug/l=C ₀	46 d	465 d	929 d
100	156	1563	3126
10	503	5030	10060
<u>Tetrachloroethene</u>			
1000 ug/l	21	210	420
100	90	900	1800
10	355	3549	7098
<u>Napthalene</u>			
1000 ug/l	23	230	460
100	80	800	1600
10	268	2682	5364
<u>Benzene</u>			
1000 ug/l	18	180	360
100	46	460	920
10	204	2036	4073
<u>1,4-Dichlorobenzene</u>			
1000 ug/l	10	100	200
100	45	450	900
10	185	1848	3696
<u>1,2-Dichloroethane</u>			
1000 ug/l	4	40	80
100	6	60	120
10	8.5	85	170

To account for the effects of mass transfer in the adsorption columns, the plug flow homogeneous surface diffusion model (PFHSDM) was used. The results of these two modelling runs for the predicted breakthrough of the six Phase II monitor compounds are plotted in Figure 1 and Figure 2. The breakthrough curves were calculated using the equilibrium isotherm parameters determined above. A water temperature of 13.8°C was assumed for both runs. Figures 1 and 2 contain plots of the breakthrough curves in one minute and ten minute EBCT columns, respectively. The model runs for the twenty minute EBCT column as influent concentration of 1000 ug/L were not successful. Modifications are in progress to resolve the numerical imitations encountered.

To simplify the modelling, the breakthrough behaviour of naphthalene was assumed to be similar to tetrachloroethene as their predicted equilibrium parameters were approximately equal. The column effluent concentration was normalized by dividing the actual effluent concentration by the influent concentration of 1000 ug/L. To separate the individual breakthrough curves more clearly, the time scale is plotted logarithmically. Although the five compounds breakthrough then column in the same relative order as predicted by equilibrium theory, the time to breakthrough (i.e. time at $C/C_0 = 0.5$) is less when accounting for mass transfer effects within the column, as was expected.

Based on these results, the proposed sampling times for the one minute EBCT column are shown as labelled vertical lines in Figure 1.

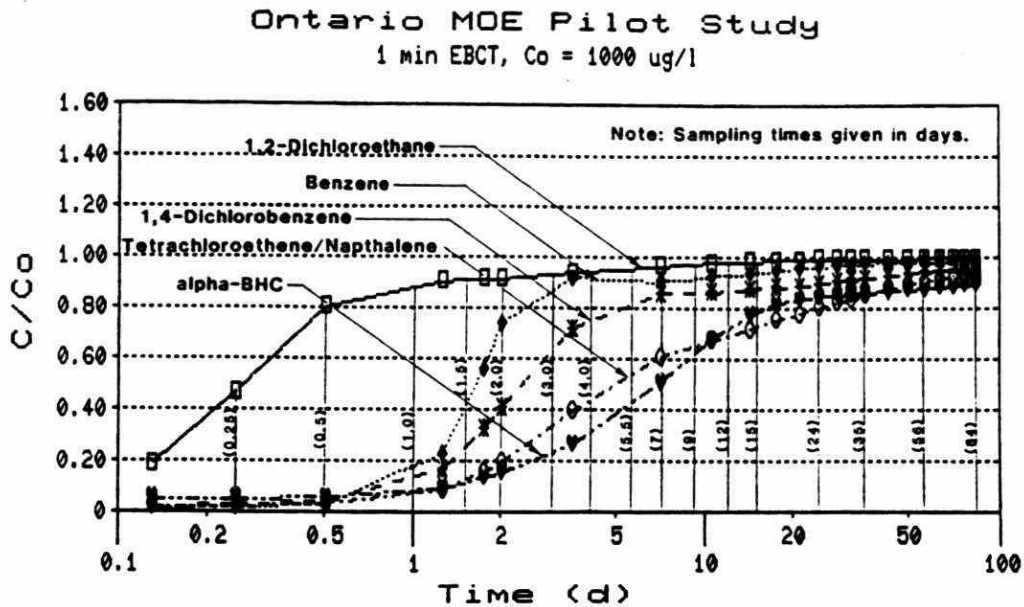


Fig. 1 HSDM 1 min. predicted breakthrough curves

The breakthroughs of the five modelled compounds in the ten minute EBCT column are plotted in Figure 2. The effects of competitive adsorption are more pronounced in this column as evidenced by the breakthrough curves of 1,2-dichloroethane and benzene. These compounds are both weakly adsorbed and breakthrough the column relatively quickly. As the other, more strongly adsorbed compounds are removed on the carbon, the dimensionless effluent concentration of 1,2-dichloroethane and benzene rises beyond 1.0, an indication of chromatographic effects.

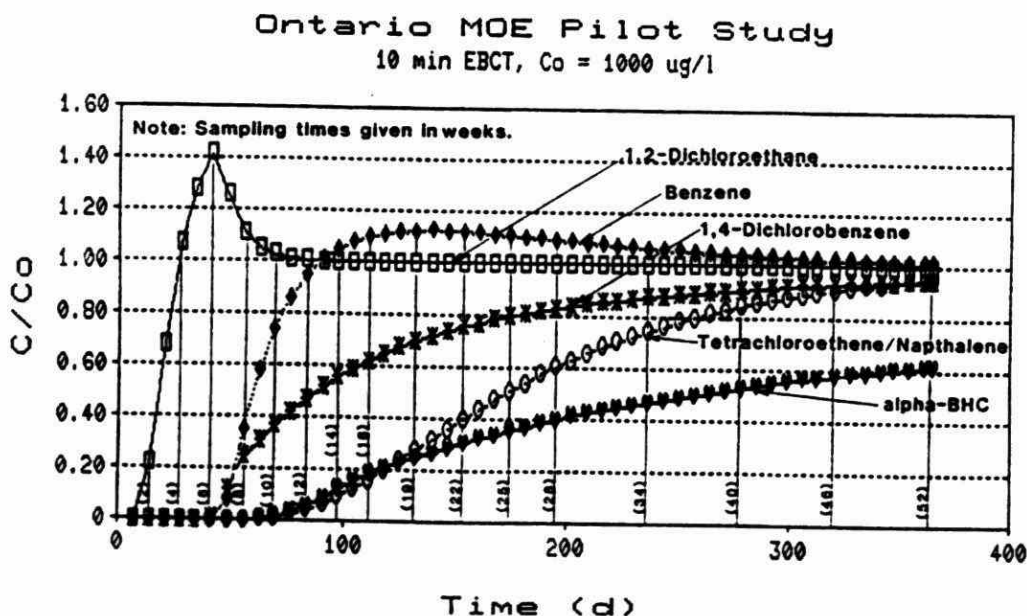


Fig. 2 HSDM 10 min. predicted breakthrough curves

Similar to Figure 1, the proposed sampling times for the ten minute EBCT column are shown as labelled vertical lines in Figure 2.

Figure 3 summarizes the sampling times for all three EBCTs. The sampling frequency for the 20 minutes EBCT column is shown in the lowest timeline.

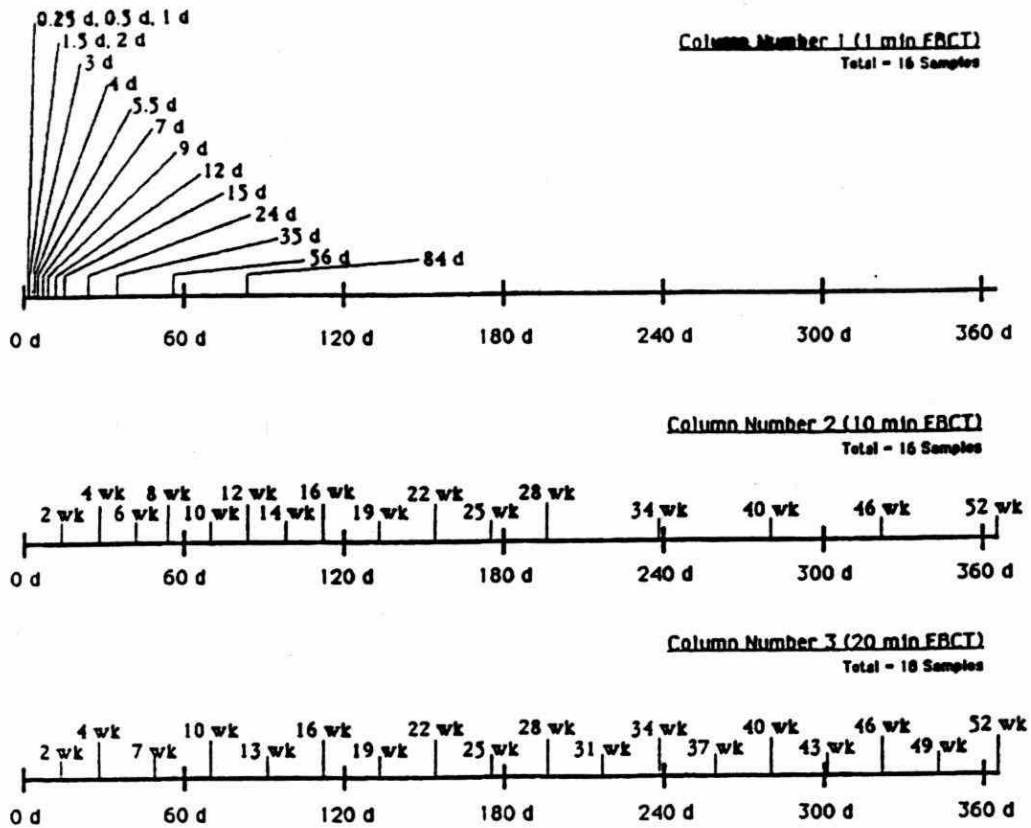


Fig. 3 Spiked GAC column sampling times

PILOT PLANT DESIGN

General Configuration and Materials of Construction. The pilot plant will model a complete water treatment process consisting of flash mixing and coagulation, flocculation, sedimentation and filtration, followed by granular activated carbon adsorption. A single treatment train is provided through filtration. After filtration there are four parallel adsorption process trains, 2 of which serve as backup, i.e. each process train is replicated once. A simplified flowsheet is shown in Fig. 4.

The first process train consists of a single adsorption vessel with a 20 minute empty bed contact time (EBCT). The second process train has three adsorption beds operating in series with EBCT of 1 minute, 9 minutes and 10 minutes each respectively.

The materials of construction as well as process equipment and instrumentation have been carefully selected so that all water-contacting surfaces throughout the entire delivery and treatment processes are of chemically inert substances (i.e. glass, teflon and stainless steel). The design criteria for the various unit

processes are described below.

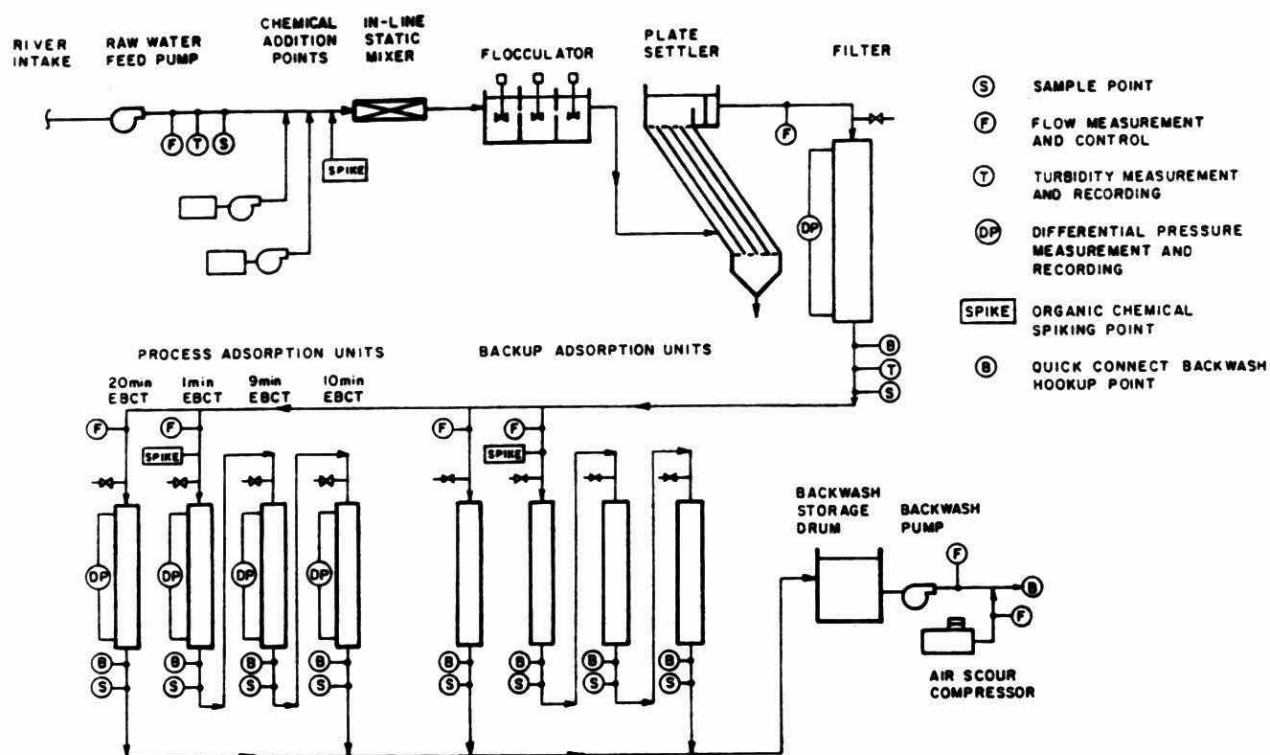


Fig. 4 Simplified pilot plant flowsheet

Raw water supply. The pilot plant is supplied with raw water from the Niagara River through the Niagara Falls Water Treatment Plant's intake system. The draw-off point is in the influent conduit after the travelling screens, but prior to the low lift suction well and the prechlorination and powdered activated carbon addition points. A dedicated stainless steel pump and supply line deliver raw water to the pilot plant, located in the low lift pumping station.

Flash mixing. Flash mixing for both the addition of coagulants, filter-aid and organic spiking compounds is done with an 8 stage Komax-type static mixer.

Flocculation. The flocculator is designed for a 3.8 L/min (1 U.S. gpm) flow. It is divided into 3 compartments, each of which has a hydraulic detention time of 10 minutes. Each compartment has an individually controlled stirrer capable of producing an energy input in the range of $G = 5$ to 30 sec^{-1} .

Sedimentation. The sedimentation process occurs in a lamella clarifier. The lamella plates are 244 cm (8 ft) long and are inclined at an angle of 55 degrees to the horizontal. The plate separation is 5.1 cm (2 inches) and plate width is approximately 23.5 (9½ inches). The overflow rate of the lamella clarifier is 4.75 m/hr (2,840 gpd/ft²).

Filtration. The filter is a 10.2 cm (4 inch) diameter column, 305 cm (10 feet) high. It is constructed from glass pipe and capped with 304 stainless steel flanges. The lower flange has a built-in plenum with a flow divider plate and stainless steel media retainer. The filter will operate at a flowrate of 12.2 m/hr (5 gpm/ft²), and will use the same media used currently at the Niagara WTP.

Carbon adsorption. The carbon adsorption contact vessels are constructed exactly as the filter with the exception that they are 7.6 cm (3 inches) in diameter. At the empty bed contact times stated above, the flow rate through each adsorption train is 0.237 L/min (0.0625 U.S. gpm).

Instrumentation. A recording turbidimeter is installed at two points in the pilot plant. These are at the entrance point for the raw water and at the filter effluent. Filter head loss is measured by a differential pressure (DP) cell. There are also DP cells on four of the eight carbon adsorption vessels. As with the turbidimeters, the DP cells are outfitted with strip chart recorders.

Organic spiking points. Spiking points for organic chemicals are located at the entrance to the flocculator and in the filter effluent, upstream of the two carbon adsorption process trains which consist of the three adsorption vessels in series.

Sampling points. Sample valves in the pilot plant are located on the raw water supply, the filter effluent and at the end of each carbon adsorption vessel. In addition, samples may be taken from the free water surfaces in the flocculator and the sedimentation tank.

DATA ANALYSIS

At the simplest level the organics removal data generated during Phases I and II will indicate the effectiveness of the chosen treatment train in removing ambient concentrations of SOC_s. Based on the currently available water quality data with respect to SOC_s, the conventional water treatment processes followed by GAC fixed bed adsorbers are expected to remove all the monitor compounds at their ambient concentrations. Although useful as demonstration, operation under these conditions for the limited period of the pilot plant study yields little information on GAC costs (i.e. the impact of EBCT on GAC usage rate and regeneration frequency) and the ability of the GAC columns to act as a barrier against shock loads of SOC_s as would occur following a spill.

The data obtained from the spiked GAC adsorption columns will be used to evaluate both these issues. Because the elevated SOC concentrations in the spiked filtered water are expected to cause breakthrough in at least one of the columns, the breakthrough curves can be used to calibrate the mass transfer adsorption model. procedure which uses a combination of the ECM and the HSDM has been developed to simplify mass transfer model calculations by reducing the number of components that need to be considered in multicomponent mass transfer calculations. Assuming that the effects of ambient DOC concentrations on the adsorption of varying concentrations of SOC_s and of the competitive adsorption of a number of SOC_s can be evaluated, the model will be useful for several purposes.

First, the model can be used to estimate the breakthrough of DOC and SOC_s at their ambient concentrations in order to set regeneration criteria. The ambient concentration depends on the effectiveness of the upstream processes. Thus, the organic loading on the carbon columns have varying ratios of DOC to SOC_s. The associated operating costs could then be calculated, assuming this were the primary function of GAC contactors.

If the primary function of GAC contactors were instead to provide a barrier against temporary high concentrations of SOC_s, as would occur during a chemical spill, the model could be used to help evaluate operating criteria. At ambient concentrations, DOC would provide the greatest loading on the carbon columns. The model could be used to evaluate the adsorption capacity remaining as a function of time. Note that the adsorption capacity remaining would also depend on

the characteristics of the spilled chemical. The wide range of physiochemical characteristics of the SOC's used in Phase II will provide useful data for evaluating a number of spill scenarios.

REFERENCES

- City of Toronto, Department of Public Health (1954). Toronto's Drinking Water: A Chemical Assessment.
- Crittenden, J.C. and colleagues (1985). Design of Fixed-Beds to Remove Multi-component Mixtures of Volatile Organic Chemicals. Presented at 1985 AWWA Meeting, June 23-27, at Washington, D.C.
- International Joint Commission (1983). Report to the Great Lakes Water Quality Board; An Inventory of Chemical Substances Identified in the Great Lakes Ecosystem. Vol. I.
- Municipality of Metropolitan Toronto, Department of Public Works (1983). Water Test Data, 1971-1983.
- Niagara River Toxics Committee (1984). Report of the Niagara River Toxics Committee.
- New York Public Interest Group (1981). The Ravaged River.
- Ontario Ministry of the Environment (1984). Drinking Water Survey of Selected Municipalities in the Niagara Area and Lake Ontario.
- Ontario Ministry of the Environment and Environment Canada (Canada-Ontario Review Board) (1985a). Trace Organics in Ontario Drinking Water Along the Niagara River.
- Ontario Ministry of the Environment (1985b). Data from MOE routine monitoring program of raw and treated water in the Niagara Falls area, 1978 to 1985.

First presented at the 2nd National Conference on Drinking Water, Edmonton, Alberta, April 1986.

THE ROLE OF ORGANIC CARBON IN CONTROLLING THE
OCCURRENCE OF DENITRIFICATION IN GROUNDWATER

R.C. Starr and R.W. Gillham

Institute for Groundwater Research
Department of Earth Sciences
University of Waterloo
Waterloo, Ontario

BACKGROUND

Nitrate is recognized as the most commonly identified groundwater contaminant (Freeze and Cherry, 1979). Decomposition of plant and animal matter, such as from barnyards and sewage disposal facilities, may result in high concentrations of nitrate in groundwater. Widespread nitrate contamination often results from the use of agricultural fertilizers. Groundwater provides drinking water in many agricultural areas, but extensive nitrate contamination can make obtaining a supply of drinking water with nitrate concentrations below the 10 mg-N/l drinking water standard difficult. Mechanisms that control nitrate concentrations in groundwater are therefore of considerable practical importance in areas where nitrate contamination is common.

Denitrification, the process by which some bacteria convert nitrate (NO_3^-) into nitric oxide (NO), nitrous oxide (N_2O) and molecular nitrogen (N_2), lowers nitrate concentrations and can therefore reduce nitrate contamination problems.

FIELD EVIDENCE OF DENITRIFICATION IN GROUNDWATER

Previous studies conducted by the University of Waterloo have

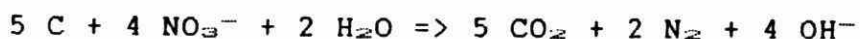
shown that denitrification occurs in some aquifers beneath agricultural land in southern Ontario. Gillham and Cherry (1978) interpreted geochemical profiles from several sites as indicating that denitrification was responsible for decreasing nitrate concentrations with depth. Trudell et al. (1985) describe an experiment in which groundwater spiked with nitrate was injected into a shallow aquifer. Nitrate concentrations declined more than could be attributed to dilution, and the population of denitrifiers increased over the course of the experiment. These results, coupled with changes in other geochemical parameters, indicate that denitrification occurred at this site. Although these studies indicate that denitrification occurs in groundwater in some settings, it is not an important mechanism in many outer aquifers. Gillham and Cherry (1978) also describe an aquifer where denitrification did not appear to occur, and the common occurrence of nitrate-contaminated groundwater suggests that denitrification does not occur, or at least that the denitrification rate is less than the rate of nitrate input, in many aquifers. An understanding of the factors that control the rate of denitrification in groundwater is required in order to predict trends in nitrate contaminated aquifers, and may provide insight into effective aquifer renovation schemes.

Two field sites in southern Ontario were characterized to develop an understanding of factors that control the occurrence and rate of denitrification on groundwater. Both sites are on the edge of active agricultural fields and receive regular applications of nitrogen fertilizer. Each is underlain by a

sandy, unconfined aquifer. Figure 1a shows geochemical profiles at the field site near Rodney, Ontario. Nitrate and chloride are believed to be derived from agricultural fertilizer, and the presence of chloride throughout the profile at fairly uniform concentrations suggests that fertilizer derived solutes were present throughout the section. The marked decline in nitrate from 25 mg-N/l to less than the 0.3 mg-N/l detection limit over a vertical distance of 0.5 metre and within 1.5 metres of the water table suggests that denitrification is an active process at this site. This is in agreement with Trudell et al. (1985), who performed their injection experiment here. In contrast, nitrate persists for nine metres below the water table and closely parallels chloride concentration at the field site near Alliston, Ontario (Figure 1b). This indicates that denitrification was not occurring at an appreciable rate in groundwater at this site.

LAB RESULTS

Denitrification is performed largely by heterotrophic bacteria that reduce nitrate and oxidize organic carbon to gain energy. The reaction may be represented in a gross sense by



where C represents organic carbon. This shows that the mass of organic carbon consumed during denitrification is comparable to the mass of nitrate reduced to nitrogen, and therefore that the availability of organic carbon can influence the amount of nitrate that can be denitrified.

A major difference between the physical characteristics of the two field sites is the depth to the water table. It is at a depth of about one metre at Rodney, but at about four metres at Alliston. Gillham and Cherry (1978) observed a pattern similar to the one shown in Figure 1, in that denitrification appeared to occur in aquifers with a water table only one or two metres below ground surface, but not to occur in aquifers with a deeper water table. They hypothesized that water table depth could influence the flux of organic carbon from the overlying unsaturated zone into the saturated zone. Oxidation of organic carbon to carbon dioxide reduces the mass of organic carbon as it is transported downward from the topsoil horizon to the underlying aquifer, so in general the flux of organic carbon into shallow water table aquifers would be expected to be greater than into deeper water table aquifers.

Figure 2 shows the concentration of dissolved organic carbon (DOC) in pore water and solid phase organic carbon (F_{oc}) at Rodney. Both profiles show that the topsoil (0-0.3 m) is a large reservoir of organic carbon. Concentrations are much lower between the topsoil and the watertable (1 m) and still lower below the watertable. In general, water at greater depth in this system has had a longer residence time, so decreasing concentrations with depth is consistent with oxidation of organic carbon during transport.

The ability of materials from various depths at Rodney to support denitrification was determined in the laboratory. The

acetylene inhibition technique (Tam and Knowles, 1976) was used, in which the concentration of nitrous oxide is proportional to the mass of nitrate denitrified. Figure 3 shows the experimental results. The control case shows little systematic variation with depth. Samples that were spiked with nitrate show much more denitrification than the control case in the upper metre, indicating that denitrification in the laboratory was limited by low nitrate availability. This is not surprising, since the cores used in this work were collected after the growing season and long after fertilized application. The denitrification rate was quite high in samples from the organic carbon rich topsoil horizon and generally lower in the vadose zone below the topsoil, and still lower below the water table. Below one metre depth there was little difference between the control and nitrate-amended samples, indicating that denitrification in these samples was not nitrate limited. A third suite of samples was spiked with both nitrate and glucose, a readily available organic carbon source for bacteria. The data for these samples coincide with those from the nitrate amended samples to a depth of one metre, indicating that abundant organic carbon was present. At greater depths, denitrification was enhanced by the addition of glucose, indicating that although sufficient organic carbon to support denitrification was present, the denitrification rate was limited by organic carbon availability.

The results of similar work with samples from Alliston are shown on Figure 4. Denitrification in the control case was high

at shallow depths and generally decreased with increasing depth. Denitrification was not observed in samples collected below two metres, and addition of nitrate did not stimulate denitrification. Glucose addition caused a substantial increase in the observed denitrification rate at all depths, indicating that the availability of organic carbon was limiting. In particular, addition of glucose to samples from greater than two metres depth caused denitrification to occur, which contrasts sharply with the lack of denitrification in these samples when glucose was not added. This clearly indicates that low availability of organic carbon inhibited denitrification in these samples.

The results from the laboratory support the hypothesis that the available mass of organic carbon decreases with depth, and that denitrification does not occur in groundwater at Alliston because too little organic carbon is available.

FIELD RESULTS

The rate of denitrification was measured insitu at both field sites as an independent measure of the importance of organic carbon. As in the laboratory work, the mass of nitrous oxide is proportional to the mass of nitrate denitrified.

Figure 5a shows the results of the control case at Rodney. The decline in nitrate coupled with the production of nitrous oxide clearly shows that denitrification occurred. This demonstrates that denitrification occurs under natural conditions

at Rodney, and that there is sufficient organic carbon to support denitrification. A second treatment was used, in which glucose was added. Figure 5b shows that the denitrification rate was enhanced by the addition of a readily usable source of organic carbon. The measured dissolved organic carbon concentrations show that the glucose was consumed between 2 and 4 days. The denitrification rate during the period when glucose was utilized was 1200 mg-N/l/year, and declined to 260 mg-N/l/year afterwards, which is quite close to the 210 mg-N/l/year observed in the control case. This indicates that sufficient natural organic carbon to support denitrification was present at Rodney, but that the rate was controlled by organic carbon availability. This agrees with the results of the laboratory investigation.

Figure 6 shows the results of similar experiments at Alliston. Denitrification was not observed in the control case, but did occur in the glucose-amended case. This shows that denitrification did not occur in the control case due to an insufficient supply of organic carbon, and is also in agreement with the laboratory results.

SUMMARY

Groundwater at both Rodney and Alliston is contaminated with nitrate at concentrations above the drinking water limit. Denitrification at Rodney consumes nitrate and nitrate concentrations fall rapidly with depth, so that only the upper 1.5 metres of the aquifer is contaminated with nitrate.

Denitrification does not occur at the Alliston field site, and high concentrations of nitrate persist for 8 metres below the watertable. This clearly shows the importance of denitrification in mitigating contamination of groundwater beneath agricultural land.

The experimental results show the importance of organic carbon availability on the occurrence and rate of denitrification in groundwater. Oxidation of organic carbon during transport through the unsaturated zone influences the organic carbon flux into the saturated zone. The insitu experiments at Alliston show that denitrification can be induced by the addition of labile organic carbon, which suggests that it may be possible to renovate some nitrate contaminated aquifers by stimulating denitrification with the addition of labile organic carbon.

REFERENCES

- 1 Freeze, R.A., and J.A. Cherry, 1979. Groundwater. Prentice-Hall, Englewood Cliffs.
- 2 Gillham, R.W., and J.A. Cherry, 1978. 'Field Evidence of Denitrification in Shallow Groundwater Flow Systems', Water Pollution Research Canada, 13, 53-71.
- 3 Tam, T.V. and R. Knowles, 1976. 'Acetylene Inhibition of Nitrous Oxide Reduction by Denitrifying Bacteria', Biochemical and Biophysical Research Communications 69(3) 705-710.
- 4 Trudell, M.R., R.W. Gillham and J.A. Cherry, 1985. 'An Insitu Study of the Occurrence and Rate of Denitrification in a Shallow Unconfined Sand Aquifer', submitted to the Journal of Hydrology.

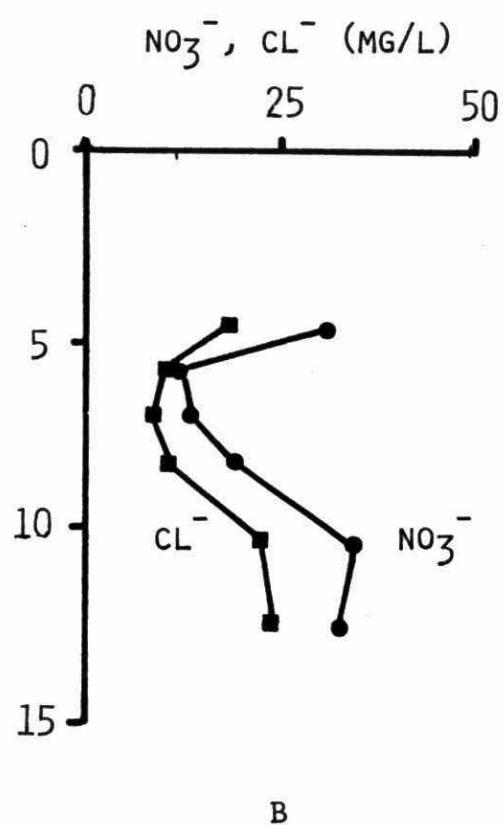
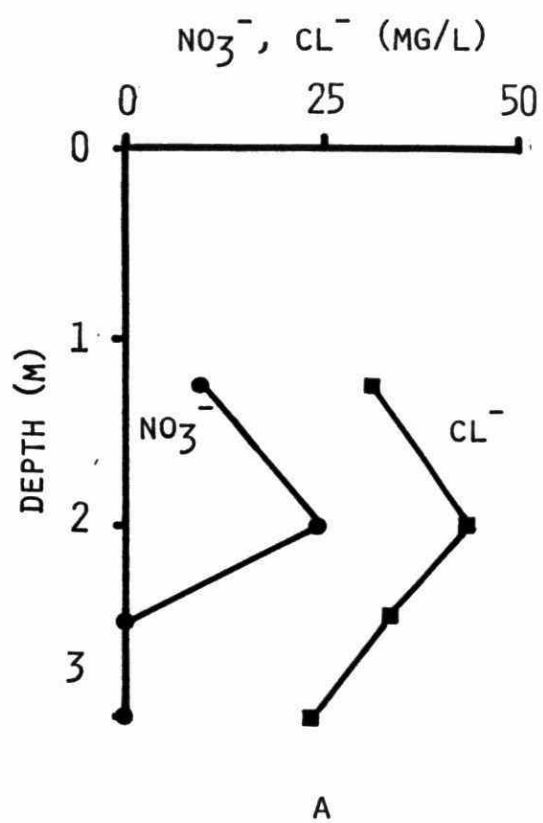


FIGURE 1
GEOCHEMICAL PROFILES
(A) RODNEY
(B) ALLISTON

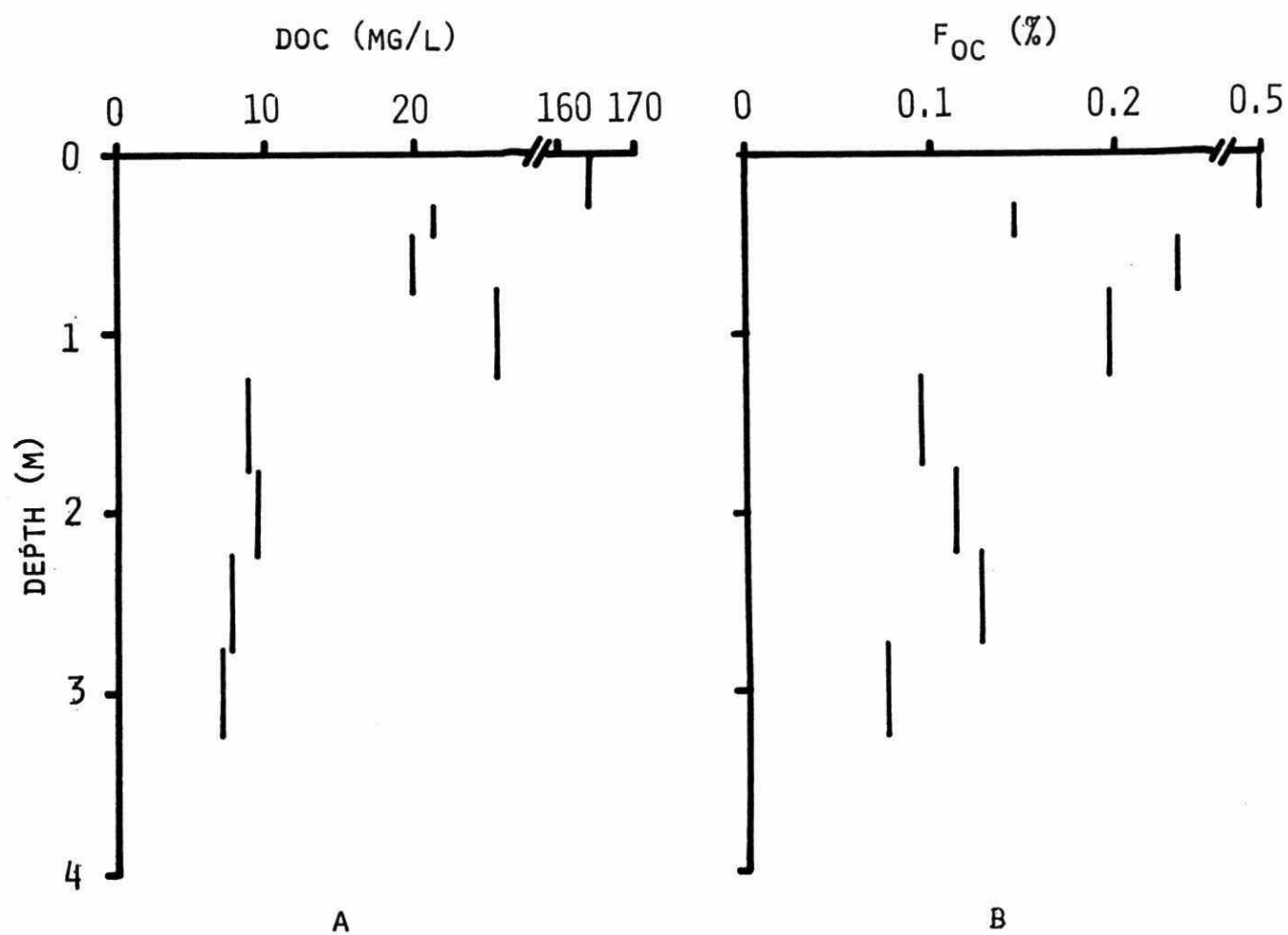


FIGURE 2

(A) DISSOLVED ORGANIC CARBON IN RODNEY POREWATER

(B) SOLID ORGANIC CARBON IN RODNEY SEDIMENT

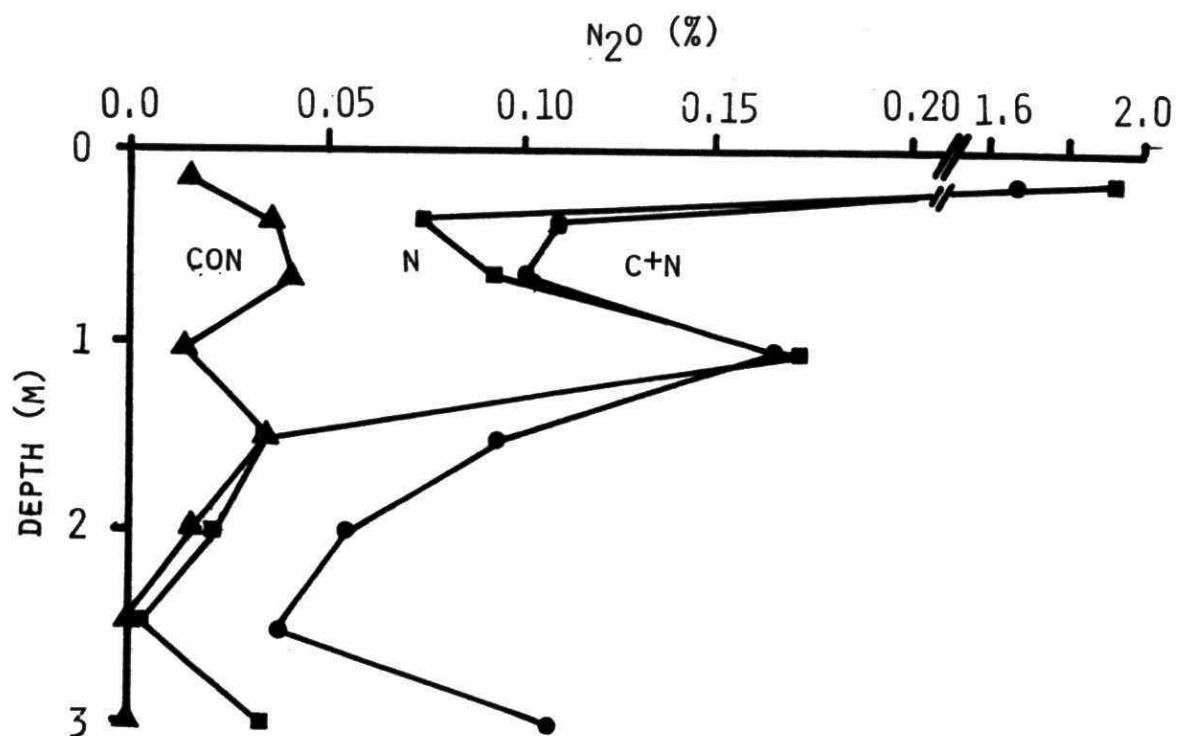


FIGURE 3
LABORATORY DENITRIFICATION TEST
RODNEY MATERIALS

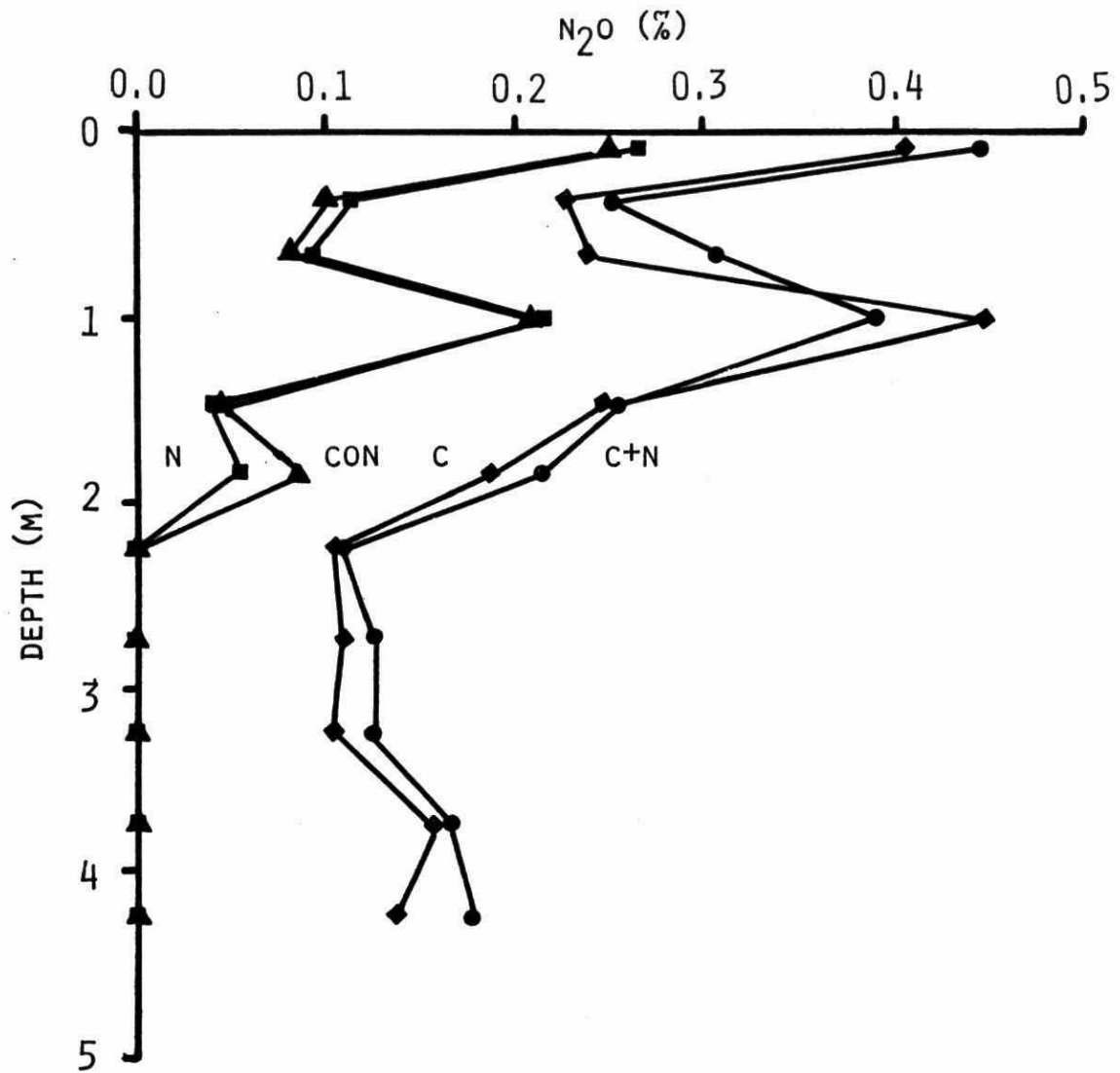


FIGURE 4
LABORATORY DENITRIFICATION TEST
ALLISTON MATERIALS

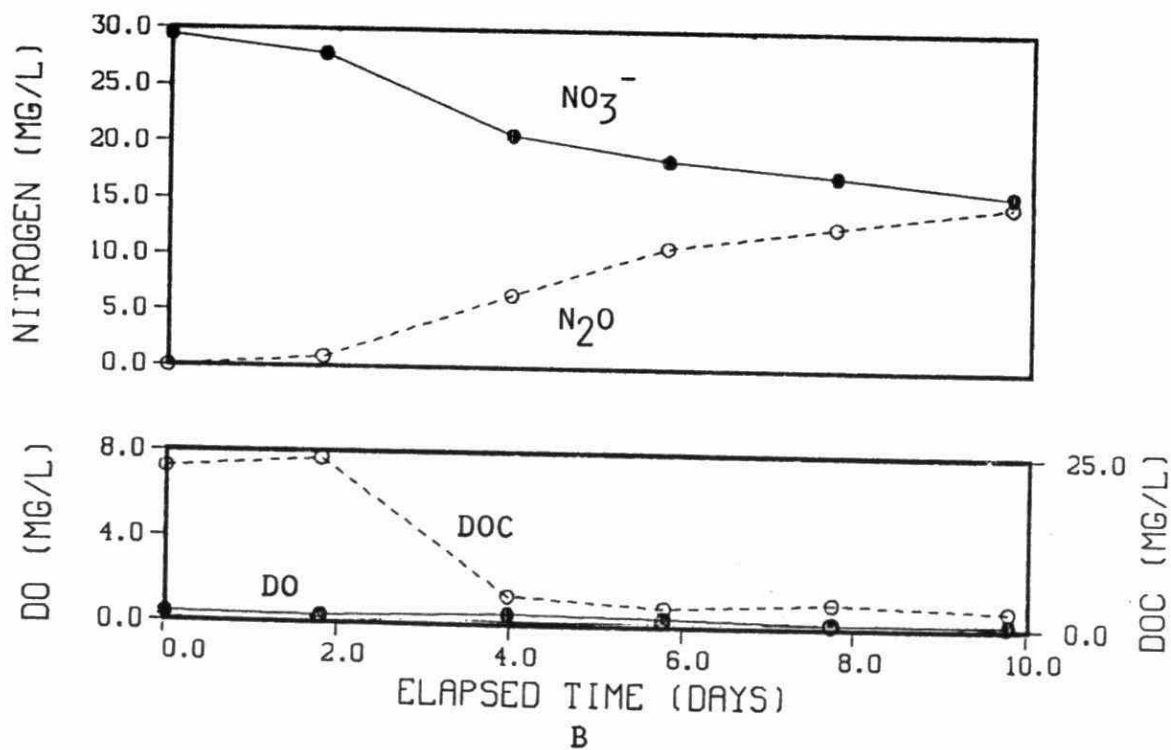
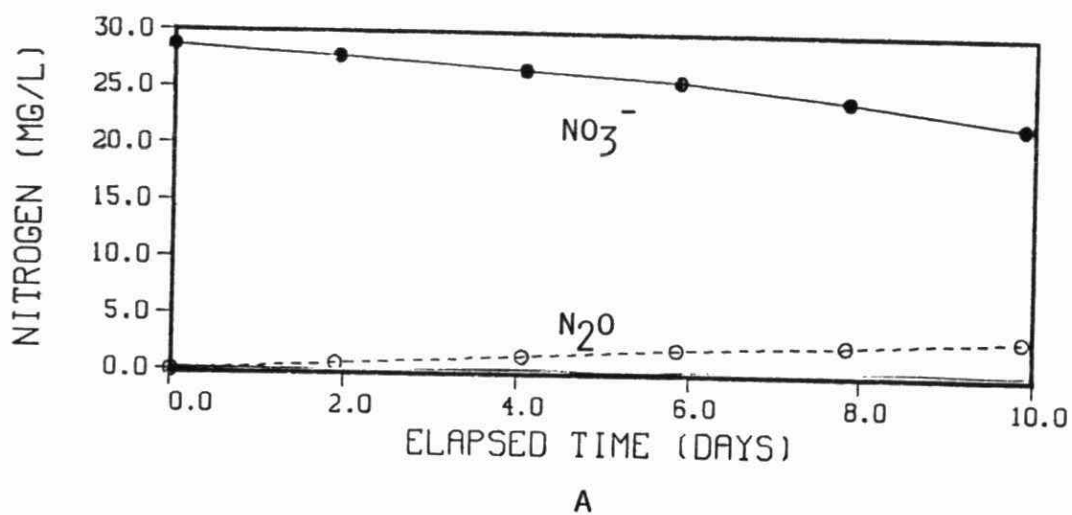


FIGURE 5
RODNEY INSITU DENITRIFICATION
(A) CONTROL
(B) GLUCOSE AMENDED

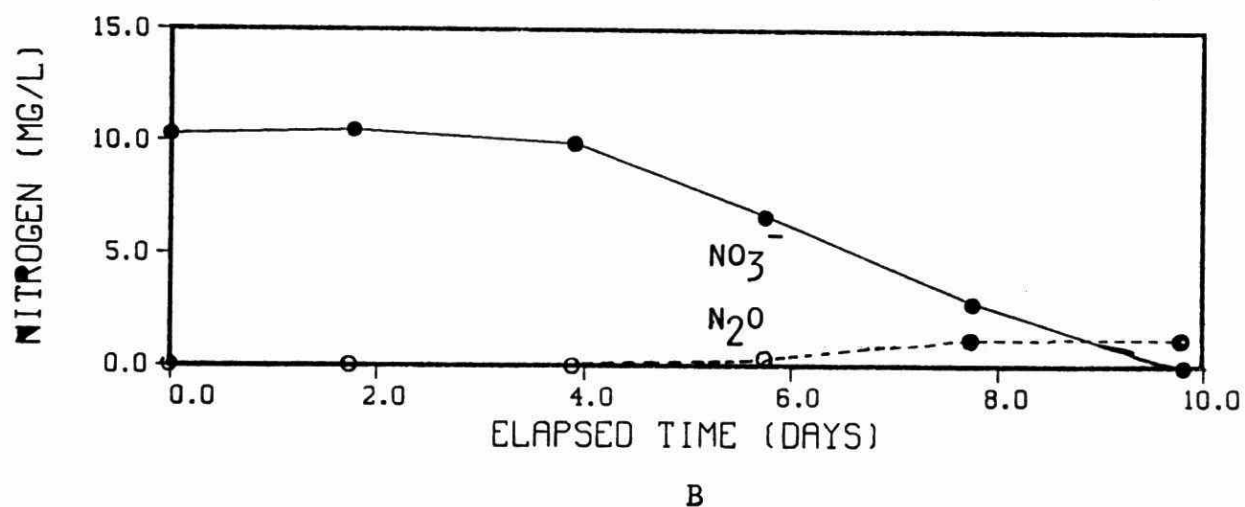
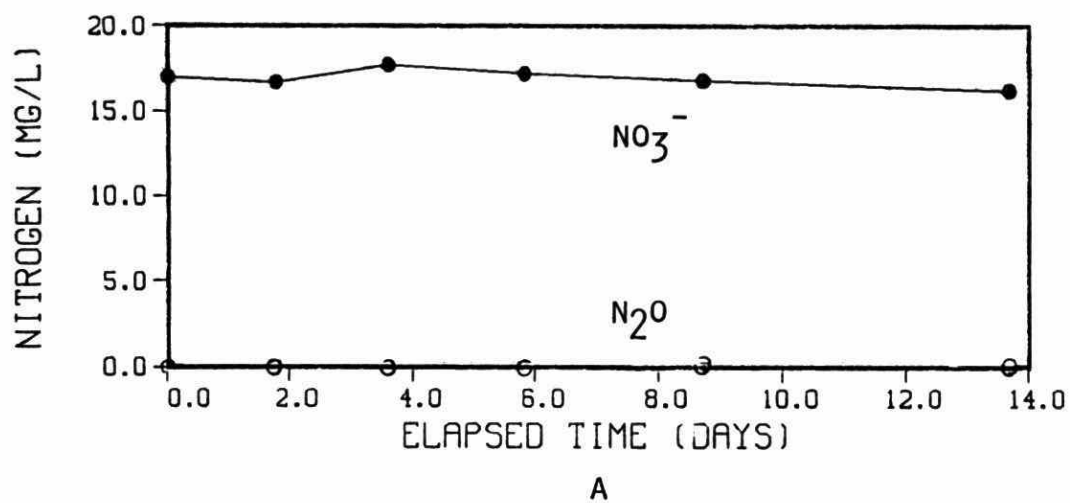


FIGURE 6
ALLISTON INSITU DENITRIFICATION
(A) CONTROL
(B) GLUCOSE AMENDED

REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO,
1980 TO 1985

James McD. Robertson, D.V.M, M.Sc.(Med.)¹

Harvey J. Chan, M.D.²

¹Associate Professor, Department of Epidemiology and Biostatistics, Faculty of Medicine, University of Western Ontario, London, ON, N6A 5C1

²Graduate Student.

Presented at the 1986 Technology Transfer Conference, Toronto, December, 1986.

ACKNOWLEDGEMENTS

This project was supported by the Ontario Ministry of Health and The Ontario Ministry of the Environment.

The assistance of Drs. L.F. Smith, P.R.W. Kendall and R. Khazen and Mrs. C. Ragos of the Ministry of Health is gratefully acknowledged as is that of Mrs. R. Gage, D. Georgas and J. Workman of the Office of the Registrar General. Dr. G.J. Sherman of the Canadian Congenital Anomalies Surveillance System provided the data on congenital anomalies. This project would not have been possible without the support and cooperation of Dr. W.A. Everett, Medical Officer of Health, Kent-Chatham Health Unit and Dr. L.M.C. Duncan, Medical Officer of Health, the Lambton Health Unit.

INTRODUCTION

The spills of various toxic substances into the St. Clair River during the six year period, 1980 to 1985, with the potential contamination of drinking water in certain communities has caused understandable concern among both the residents and the Medical Officers of Health in Kent and Lambton Counties. Although no acute effects have been documented to date, the possibility of adverse effects in pregnant women and their children cannot be ignored. Unlike neoplastic and other chronic diseases, adverse reproductive and first-year-of-life outcomes could provide a highly sensitive, rapidly-occurring and easily documented sentinel measure of the risk of exposure to potentially contaminated drinking water in these counties. With this in mind, the Ontario Ministry of Health issued a call for proposals for epidemiologic studies in early 1985. The study described here was designed to document the presence/absence and extent of the risks of abnormal pregnancy and first-year-of-life outcomes in women and their children whose source of drinking water during the six year period, 1980 to 1985, was the St. Clair River.

METHODS

The study has three phases: an ecologic study, a case-control study, and a retrospective, special exposure cohort study. Drinking water drawn from the St. Clair River is the primary exposure of interest. The outcomes selected for study are listed in Table I.

1. Ecologic study

This phase of the study will compare the incidence rates of the abnormal outcomes during the six year period, 1980 to 1985, in Kent and Lambton Counties with those of the Ontario Southwest Region (Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties) and with those of the Province to determine if any of the outcomes occurred in excess in the index counties. Comparisons will also be made between exposed and unexposed groups, defined by geographic location, within Kent and Lambton Counties.

Six year total incidence rates will be calculated from data supplied by the Ontario Ministry of Health. The comparisons will be based on relative risks estimates with corresponding 95 per cent confidence limits.

2. Case-control study

This phase will focus on stillbirths, congenital anomalies, low birth weight ($\leq 1,500$ gm.) and first-year-of-life outcomes which occurred between 1 January, 1980 and 31 December, 1985. We excluded spontaneous abortions because the number, almost 800

in 1980 to 1984, was too large to include in an interview study given the time frame and funding of the project. Taking into account combined diagnoses for example, stillbirth and congenital anomaly, we estimate that some 500 cases will be eligible for interview.

The controls will be a group of women from Kent and Lambton Counties who had normal babies in the same time period or whose children were normal and survived beyond the first year of life. Control mothers will be individually matched to case mothers on maternal age (± 1 year), parity, multiple birth and sex of the child.

Cases and controls will be interviewed at home using a pre-tested interview schedule to gather information on the variables listed in Appendix 1.

The primary analysis will concentrate on case-control differences in exposure to drinking water from the St. Clair River. Comparisons of frequencies will be made using the marginal Chi square test. The effects of confounding variables will be controlled by stratification or paired multiple logistic regression analysis where appropriate. Since this is a population-based case-control study, it will also be possible to calculate relative and attributable risks directly from the data.

3. Retrospective, special exposure cohort study

Some 40 chemical spills into the St. Clair River between 1980 and the end of 1985 have been documented. We have selected

six such spills (Table II), on the basis of time period, material spilled and amount spilled, for further study. Using spontaneous abortions, stillbirths, congenital anomalies and low birth weight, we shall attempt to estimate the influence of these spills on outcomes of pregnancy.

A cohort of women who were pregnant at the time of these spills and, based on place of residence, were considered to be exposed will be assembled. The outcomes of their pregnancies will be compared with those of three groups of women defined as nonexposed. The comparison cohorts will include:

1. Women resident in the same places as members of the exposed cohort whose pregnancies occurred at times when they could not have been exposed to water during the selected spills.
2. An individually-matched (age, parity, multiple birth and sex of the child) cohort of women resident in Kent and Lambton Counties who were pregnant at the same time as the exposed cohort and were not exposed to water from the St. Clair River.
3. Women resident in Elgin, Huron and Middlesex Counties whose pregnancies occurred at the same time as those of the exposed cohort.

We estimate that a total of 2,000 pregnancies occurred in potentially exposed women in the entire six year period. Investigating only those pregnancies considered to be at risk of exposure to the designated spills will reduce the number

to be studied.

The exposure status of the exposed cohort and of nonexposed cohorts 1 and 2 will be confirmed by brief telephone interviews.

Incidence rates of the abnormal outcomes in the exposed cohort will be compared with those of the nonexposed cohorts to evaluate the effects of exposure during the specific spills. Relative risks with 95 per cent confidence limits will be estimated.

PRELIMINARY RESULTS

The preliminary results of the ecologic analyses for the five year period, 1980-1984 are presented in Appendix 2, Tables 1 through 3.3.1. We expect to have the provisional figures for 1985 in the near future. Spontaneous abortions are not included in these tables because data with which to calculate denominators of the rates have only recently become available.

Statistically significant differences in the frequencies of the outcomes of interest were evident only in the exposed group from Kent County. These results are summarized in Tables III and IV. Both stillbirths and perinatal deaths occurred at rates lower than those of the Ontario Southwest Region and the Province as a whole. Since the incidence rate of early neonatal deaths was elevated in the exposed group (Appendix 2, Table 3.1.1), the deficit in stillbirths must account for the deficit in perinatal deaths. The significant increase in low birth weight babies, 1,501 to 2,499 gm., was paralleled by a non-significant increase in babies weighing 1,500 gm. and under (Appendix 2, Table 2.1.1.).

Although they were statistically non-significant certain other observations are worth mentioning. The exposed group in Kent County showed consistently decreased risks of congenital anomalies one of which bordered on significance (Appendix 2, Table 1.2.1). Early neonatal deaths, neonatal deaths and infant deaths all showed consistently high relative risks with upper 95 per cent confidence limits greater than 2 in all but one

instance. The major contributor to this appeared to be the early neonatal deaths (Appendix 2, Table 3.1.1.). Since these results are incomplete, we do not believe that they warrant discussion at this time.

Since we have only recently acquired from the Ministry of Health the tape from which we shall draw our control samples for both the case-control and cohort studies, no results are as yet available. We project that the interviewing will start about mid-November, 1986 and that data gathering will be completed by mid-February, 1987. The first draft of the final report will be completed by April 30th, 1987.

Table I.

Abnormal pregnancy and first-year-of-life outcomes chosen
for study, Kent and Lambton Counties, 1980-1985.

Outcomes	I.C.D. No. ¹
<u>Pregnancy</u>	
1. Spontaneous abortion	634.0-634.9
2. Stillbirth	-----
3. Live, low birth weight: $\leq 1,500$ gm. 1,501-2,499gm.	765.0
4. Congenital anomalies	
Anencephalus	740.0-740.2
Spina bifida	741.0-741.9
Hydrocephalus	742.3
Congenital heart disease	745.0-747.9
Cleft palate and cleft lip	749.0-749.2
Tracheo-esophageal fistula, esophageal atresia and stenosis	750.3
Atresia and stenosis of large intestine, rectum and anal canal	751.2
Hypospadias and epispadias	752.6
Reduction deformities of upper and lower limbs	755.2-755.4
Down's syndrome	758.0
<u>First-year-of-life</u>	
1. Early neonatal death, 0-6 days	-----
2. Neonatal death, 0-27 days	-----
3. Perinatal death, 0-6 days plus stillbirth	-----
4. Infant death, 0-1 year	-----

¹International Classification of Diseases, 9th Revision, 1979.

Table II.

Selected¹ chemical spills into the St. Clair River,
1980 to 1985.

Year Month Day	Location	Material	Amount metric tons	Recovered Per cent
80-01-08	Sarnia	Bunker C oil	21	38
81-12-21	Sarnia	Bunker C oil	21	81
84-02-22	Sarnia	No. 2 oil	116	80
84-02-27	Sarnia	No. 2 oil	16	81
85-08-13-16	Sarnia	Perchloroethylene	54	100
85-12-19	Sarnia	Isobutylene wash water	26	0

¹Selection was based on: the date of the spill and the material and amount involved.

Table III.

Statistically significant ($P < 0.05$) risks of stillbirth, low birth weight and perinatal death in the exposed group¹, Kent County relative to the Ontario Southwest Region (OSWR)² and the Province of Ontario (ON), 1980-1984.

Outcome	Comparison areas			
	OSWR-1	OSWR-2 ³	ON-1	ON-2 ³
<hr/>				
Stillbirth				
Risk ⁴	0.30	0.30	0.30	0.30
Limits ⁵	0.10-0.93	0.10-0.93	0.10-0.93	0.10-0.93
Birth weight 1,501-2,499 gm.				
Risk	1.32	1.32	1.29	1.29
Limits	1.07-1.63	1.07-1.63	1.05-1.59	1.05-1.59
Perinatal Death ⁶				
Risk	0.77	0.76	0.78	0.78
Limits	0.63-0.94	0.62-0.92	0.65-0.94	0.65-0.94

¹Wallaceburg and Tilbury.

²The Ontario Southwest Region includes: Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties.

³Excluding Kent and Lambton Counties.

⁴Ratios of the incidence rates in the exposed group, Kent County to those of the areas indicated.

⁵95 per cent confidence limits of the relative risk estimates.

⁶Stillbirths plus deaths 0-6 days.

Table IV.

Statistically significant ($P < 0.05$) risks of stillbirth and low birth weight in the exposed group¹ relative to the nonexposed group, Kent County, 1980-1984.

Outcome	Risk ⁴	Limits ⁵
Stillbirth	0.28	0.09-0.89
Birth weight 1,501-2,499 gm.	1.30	1.03-1.64

^{1,4,5}See Footnotes, Table III.

Appendix 1

REPRODUCTIVE OUTCOMES IN SOUTHWESTERN ONTARIO
1980 to 1985

J. McD. Robertson and H. J. Chan
Dept. of Epidemiology and Biostatistics
The University of Western Ontario

Summary of interview questions

Phase 2 -

1. Identifying data.
2. Time and place of birth of respondent and her parents.
3. Marital status, education, income.
4. Occupation of respondent and spouse.
5. Illnesses, X-rays, ultra sound examinations, prescription and non-prescription medications during the index pregnancy.
6. Cigarette smoking and alcohol, coffee and tea consumption during the index pregnancy.
7. Source of drinking water during the index pregnancy.
8. Consumption of water, drinks reconstituted with water and ice cubes during the index pregnancy.
9. Selected dietary items consumed during the index pregnancy.
10. Use of oral contraceptives prior to the index pregnancy.
11. Outcomes of previous and subsequent pregnancies.
12. Supplementary CONFIDENTIAL questionnaire to be completed by the respondent in private and returned to the interviewer in a sealed envelope.
 - 12.1 Sexually-transmitted diseases prior to the index pregnancy.
 - 12.2 Usual method of contraception prior to the index pregnancy.
 - 12.3 Use of "recreational drugs" during the index pregnancy.

Appendix 2

Table 1.

Total incidence of stillbirth and selected congenital anomalies,
Kent and Lambton Counties, the Ontario Southwest Region (OSWR)¹
and the Province of Ontario (ON), 1980-1984.

Area	Total Births Number	Stillbirths		Congenital anomalies ²	
		Number	Rate ³	Number	Rate
Kent County	8,424	56	6.6	48	5.7
Lambton County	9,813	62	6.3	53	5.4
OSWR-1	94,747	659	7.0	491	5.2
OSWR-2 ⁴	76,510	541	7.1	390	5.1
ON-1	632,972	4,510	7.1	3,371	5.3
ON-2 ⁴	614,735	4,392	7.1	3,270	5.3

¹The Ontario Southwest Region includes: Bruce, Elgin, Essex, Grey, Huron, Kent, Lambton, Middlesex, Oxford and Perth Counties.

²See Table I for a list of diagnoses.

³Rate per 1,000 total births.

⁴Excluding Kent and Lambton Counties.

Table 1.1

Relative risks¹ of stillbirth, Kent and Lambton Counties,
1980-1984.

Stillbirths				
Comparison area	Kent County		Lambton County	
	Risk	Limits ²	Risk	Limits ²
OSWR-1	0.94	0.725-1.219	0.90	0.687-1.179
OSWR-2	0.93	0.710-1.218	0.89	0.679-1.166
ON-1	0.93	0.717-1.206	0.89	0.686-1.154
ON-2	0.93	0.717-1.206	0.89	0.686-1.154
Kent vs. Lambton	1.05	0.733-1.505	--	-----

¹Ratio of the total incidence rates in Kent and Lambton Counties to those of the areas indicated.

²95 per cent confidence limits of the relative risk estimates.

Table 1.1.1.

Total incidence and relative risks¹ of stillbirth in exposed and nonexposed groups, Kent County, 1980-1984.

Stillbirths - Kent County						
Comparison area	Rate ³	Exposed ⁴		Rate	Nonexposed	
		Risk	Limits ²		Risk	Limits
	2.1	--	---	7.6	--	---
OSWR-1		0.30*	0.097-0.929		1.09	0.824-1.442
OSWR-2		0.30*	0.097-0.929		1.07	0.809-1.416
ON-1		0.30*	0.097-0.929		1.07	0.817-1.402
ON-2		0.30*	0.097-0.929		1.07	0.817-1.402
Exposed vs. Nonexposed		0.28*	0.088-0.893		--	----
Nonexposed vs. Lambton		1.21	0.836-1.752		--	----

^{1,2}See Footnotes, Table 1.1.

³See Footnotes, Table 1.

⁴Wallaceburg and Tilbury.

*Significantly different from 1, $P < 0.05$.

Table 1.2.

Relative risks¹ of congenital anomalies, Kent and Lambton Counties, 1980-1984.

Comparison area	Kent County		Lambton County	
	Risk	Limits ²	Risk	Limits
OSWR-1	1.10	0.815-1.485	1.04	0.786-1.376
OSWR-2	1.12	0.830-1.512	1.06	0.793-1.417
ON-1	1.08	0.816-1.429	1.02	0.779-1.336
ON-2	1.08	0.816-1.429	1.02	0.779-1.336
Kent vs. Lambton	1.06	0.718-1.566	--	-----

^{1,2}See Footnotes, Table 1.1.

Table 1.2.1.

Total incidence and relative risks¹ of congenital anomalies in exposed and nonexposed groups, Kent County, 1980-1984.

Congenital anomalies-Kent County						
Comparison area	Rate ³	Exposed ⁴		Rate	Nonexposed	
		Risk	Limits ²		Risk	Limits
	3.6	--	---	6.1	--	--
OSWR-1		0.69	0.286-1.664		1.17	0.858-1.595
OSWR-2		0.71	0.294-1.712		1.20	0.880-1.636
ON-1		0.68	0.282-1.639		1.15	0.852-1.552
ON-2		0.68	0.282-1.639		1.15	0.852-1.552
Exposed vs. Nonexposed		0.59	0.235-1.480		--	-----
Exposed vs. Lambton		0.67	0.449-1.000		--	-----

¹⁻⁴See Footnotes, Table 1.1.1.

Table 2.

Live births by birth weight, Kent and Lambton Counties, the Ontario Southwest Region (OSWR)¹ and the Province of Ontario (ON), 1980-1984.

Area	Total Number	Unknown Number	Live births					
			≤ 1,500gm.		1,501-2,499gm.		≥ 2,500gm.	
			Number	Rate ²	Number	Rate	Number	Rate
Kent County	8,368	0	80	9.6	412	49.2	7,876	941.2
Lambton County	9,751	1	85	8.7	442	45.3	9,223	945.9
OSWR-1	94,088	16	801	8.5	4,341	46.1	88,930	945.2
OSWR-2	75,969	15	636	8.4	3,487	45.9	71,831	945.5
ON-1	628,462	190	5,422	8.6	29,656	47.2	593,194	943.6
ON-2	610,343	189	5,257	8.6	28,802	47.2	576,095	943.9

¹See Footnote 1, Table 1.

²Rate per 1,000 live births.

Table 2.1.

Relative risks¹ of low birth weight, Kent and Lambton
Counties, 1980-1984.

Low birth weight

Comparison area	Kent County		Lambton County	
	Risk	Limits ²	Risk	Limits ²
<u>≤ 1,500gm.</u>				
OSWR-1	1.13	0.898-1.422	1.02	0.819-1.289
OSWR-2	1.14	0.906-1.435	1.04	0.826-1.309
ON-1	1.12	0.899-1.396	1.01	0.819-1.246
ON-2	1.12	0.899-1.396	1.01	0.819-1.246
Kent vs. Lambton	1.10	0.815-1.485	--	-----
<u>1,501 to 2,499gm.</u>				
OSWR-1	1.07	0.978-1.171	0.98	0.887-1.083
OSWR-2	1.07	0.968-1.183	0.99	0.896-1.094
ON-1	1.04	0.941-1.149	0.96	0.877-1.050
ON-2	1.04	0.941-1.149	0.96	0.877-1.050
Kent vs. Lambton	1.09	0.957-1.241	--	-----

^{1,2}See Footnotes, Table 1.1.

Table 2.1.1.

Total incidence and relative risks¹ of low birth weight
in exposed and nonexposed groups, Kent County, 1980-1984

Low birth weight - Kent County

Comparison area	Rate ³	Exposed ⁴		Rate	Nonexposed	
		Risk	Limits ²		Risk	Limits
<hr/>						
≤ 1,500gm.						
	11.4	--	---	9.2	--	---
OSWR-1		1.34	0.821-2.187		1.08	0.841-1.387
OSWR-2		1.36	0.833-2.220		1.09	0.840-1.414
ON-1		1.33	0.815-2.171		1.07	0.833-1.374
ON-2		1.33	0.815-2.171		1.07	0.833-1.374
Exposed vs. Nonexposed		1.24	0.715-2.149		--	-----
Exposed vs. Lambton		1.31	0.771-2.226		--	-----
<hr/>						
1,501-2,499gm.						
	60.8	--	---	46.9	--	---
OSWR-1		1.32*	1.070-1.628		1.02	0.914-1.139
OSWR-2		1.32*	1.070-1.628		1.02	0.914-1.139
ON-1		1.29*	1.046-1.591		0.99	0.887-1.105
ON-2		1.29*	1.046-1.591		0.99	0.887-1.105
Exposed vs. Nonexposed		1.30*	1.033-1.636		--	-----
Nonexposed vs. Lambton		1.04	0.904-1.196		--	-----

^{1,2,4,*}See Footnotes, Table 1.1.1.

³See Footnote 2, Table 2.

Table 3.

Total incidence of adverse first-year-of-life outcomes, Kent and Lambton Counties, the Ontario Southwest Region (OSWR)¹ and the Province of Ontario (ON), 1980-1984.

Area	Early neonatal deaths ³		Neonatal deaths ⁴		Perinatal deaths ⁵		Infant deaths ⁶	
	Number	Rate ²	Number	Rate	Number	Rate	Number	Rate
Kent County	40	4.8	46	5.5	96	11.4	80	9.6
Lambton County	54	5.5	58	5.9	116	11.8	95	9.7
OSWR-1	485	5.1	550	5.8	1,144	12.1	884	9.4
OSWR-2	391	5.1	446	5.9	932	12.2	709	9.3
ON-1	3,026	4.8	3,513	5.6	7,536	11.9	5,312	8.5
ON-2	2,932	4.8	3,409	5.6	7,324	11.9	5,137	8.4

¹See Footnote 1, Table 1.

²Rate per 1,000 live births.

³Deaths, 0 to 6 days of age.

⁴Deaths, 0 to 27 days of age.

⁵Stillbirths plus early neonatal deaths.

⁶Deaths, 0 to 1 year of age.

Table 3.1.

Relative risks¹ of neonatal death, Kent and Lambton Counties, 1980-1984.

<u>Comparison area</u>	<u>Kent County</u>		<u>Lambton County</u>	
	<u>Risk</u>	<u>Limits²</u>	<u>Risk</u>	<u>Limits²</u>
<u>Early neonatal deaths</u>				
OSWR-1	0.94	0.683-1.294	1.08	0.816-1.429
OSWR-2	0.94	0.683-1.294	1.08	0.816-1.429
ON-1	1.00	0.733-1.363	1.15	0.878-1.507
ON-2	1.00	0.733-1.363	1.15	0.878-1.507
Kent vs. Lambton	0.87	0.577-1.311	--	-----
<u>Neonatal deaths</u>				
OSWR-1	0.95	0.704-1.282	1.02	0.779-1.336
OSWR-2	0.93	0.689-1.255	1.00	0.763-1.310
ON-1	0.98	0.733-1.310	1.05	0.810-1.362
ON-2	0.98	0.733-1.310	1.05	0.810-1.362
Kent vs. Lambton	0.93	0.630-1.374	--	-----

^{1,2}See Footnotes, Table 1.1

Table 3.1.1

Total incidence and relative risks¹ of neonatal death in exposed and nonexposed groups, Kent County, 1980-1984.

Neonatal deaths-Kent County						
Comparison area	Rate ³	Exposed ⁴		Rate	Nonexposed	
		Risk	Limits ²		Risk	Limits
<u>Early neonatal deaths</u>						
	7.1	--	---	4.3	--	---
OSWR-1		1.39	0.748-2.584		0.84	0.580-1.216
OSWR-2		1.39	0.740-2.610		0.84	0.580-1.216
ON-1		1.48	0.796-2.751		0.90	0.628-1.290
ON-2		1.48	0.796-2.751		0.90	0.628-1.290
Exposed vs. Nonexposed		1.65	0.811-3.356		--	-----
Exposed vs. Lambton		1.29	0.660-2.521		--	-----
<u>Neonatal deaths</u>						
	7.1	--	---	5.2	--	---
OSWR-1		1.22	0.656-2.268		0.90	0.641-1.264
OSWR-2		1.20	0.646-2.231		0.88	0.626-1.236
ON-1		1.27	0.683-2.361		0.93	0.669-1.294
ON-2		1.27	0.683-2.361		0.93	0.669-1.294
Exposed vs. Nonexposed		1.37	0.680-2.759		--	-----
Exposed vs. Lambton		1.20	0.614-2.345		--	-----

^{1,2,4}See Footnotes, Table 1.1.1.

³See Footnote 2, Table 2.

Table 3.2

Relative risks¹ of perinatal death, Kent and Lambton
Counties, 1980-1984.

Perinatal Deaths

Comparison area	Kent County		Lambton County	
	Risk	Limits ²	Risk	Limits
OSWR-1	0.94	0.762-1.160	0.98	0.810-1.190
OSWR-2	0.93	0.754-1.147	0.97	0.802-1.173
ON-1	0.96	0.786-1.173	0.99	0.827-1.185
ON-2	0.96	0.786-1.173	0.99	0.827-1.185
Kent vs. Lambton	0.97	0.740-1.271	--	-----

^{1,2}See Footnotes, Table 1.1.

Table 3.2.1

Total incidence and relative risks¹ of perinatal death
in exposed and nonexposed groups, Kent County
1980-1984.

Perinatal deaths-Kent County						
Comparison area	Rate ³	Exposed ⁴		Rate	Nonexposed	
		Risk	Limits ²		Risk	Limits
	9.3	--	---	11.8	--	---
OSWR-1		0.77*	0.630-0.940		0.98	0.786-1.221
OSWR-2		0.76*	0.622-0.923		0.97	0.778-1.209
ON-1		0.78*	0.645-0.943		0.99	0.794-1.234
ON-2		0.78*	0.645-0.943		0.99	0.794-1.234
Exposed vs. Nonexposed		0.79	0.591-1.056		--	-----
Exposed vs. Lambton		0.79	0.609-1.025		--	-----

1-4 See Footnotes, Table 1.1.1.

Table 3.3.

Relative risks¹ of infant death, Kent and Lambton Counties,
1980-1984.

Infant Deaths

Comparison area	Kent County		Lambton County	
	Risk	Limits ²	Risk	Limits
OSWR-1	1.02	0.810-1.284	1.03	0.835-1.271
OSWR-2	1.03	0.818-1.296	1.04	0.843-1.283
ON-1	1.13	0.907-1.408	1.14	0.933-1.392
ON-2	1.14	0.915-1.421	1.15	0.942-1.405
Kent vs. Lambton	0.99	0.733-1.336	--	-----

^{1,2}See Footnotes, Table 1.1.

Table 3.3.1

Total incidence and relative risks¹ of infant death in exposed and nonexposed groups, Kent County, 1980-1984.

Infant deaths-Kent County						
Comparison area	Rate ³	Exposed ⁴		Rate	Nonexposed	
		Risk	Limits ²		Risk	Limits
	11.4	--	---	9.2	--	---
OSWR-1		1.21	0.741-1.975		0.99	0.771-1.271
OSWR-2		1.23	0.754-2.008		0.99	0.763-1.284
ON-1		1.34	0.812-2.187		1.08	0.841-1.387
ON-2		1.36	0.833-2.220		1.10	0.857-1.412
Exposed vs. Nonexposed		1.24	0.715-2.149		--	-----
Exposed vs. Lambton		1.18	0.695-2.005		--	-----

¹⁻⁴See Footnotes, Table 1.1.1.

Organic Contaminant Structure-Property - Toxicity Relationships
for Aquatic Organisms:

A Discussion of Correlations for Narcosis in Aquatic Species

Scott Abernethy

Donald Mackay

Institute for Environmental Studies,

University of Toronto,

Toronto, Ontario

M5S 1A4

ABSTRACT

A hypothesis is presented that narcosis in aquatic organisms occurs when the chemical agent achieves a certain volume fraction (estimated to be 0.63%) in the target phase. If this hypothesis is accepted, it becomes possible to estimate and correlate target-octanol and target-water partition coefficients. Novel methods of presenting QSARs based on these partition coefficients are suggested. The hypothesis is tested on four sets of data totalling 153 determinations of narcosis on fathead minnows, guppies, Daphnia magna and Artemia with satisfying results. It is suggested that the target-water partitioning characteristics are such that a "cut off" is reached for chemicals in a series of increasing molecular volume, beyond which the chemicals are not able to achieve the required water concentration necessary to establish the volume fraction at the target which causes narcosis.

INTRODUCTION

The mechanism by which a large class of organic chemicals exerts toxic effects on aquatic organisms has been described as a non-specific narcotic or anaesthetic action, with a potency controlled by the organism-water partitioning properties of the chemical. These partitioning properties are in turn controlled by the affinity of the chemical for the water and organic phases, i.e. on activity coefficients or solubilities. A number of QSARs have been developed relating LC50s or EC50s to descriptors such as octanol-water partition coefficient (K_{OW}) or water solubility (eg. Abernethy et al., 1985; 1986).

The actual narcotic mechanism remains unclear but it appears that the effect is exerted when a target site accumulates a sufficient volume of chemical to interfere with normal structure and functions. Support for this hypothesis comes from several sources.

In 1939 Ferguson suggested that equal degrees of narcosis were produced when chemicals had similar activities rather than concentrations. Equal activity (expressed as a fraction of chemical solubility) implies equal concentration in phases in which the chemical behaves ideally. If the target site is "ideal" then Ferguson's theory corresponds to approximately equal chemical concentration at the target.

In 1954 Mullins discussed the same principle and introduced a correction for molecular size, the implication being that chemicals of larger molar volume are more potent because at equal molar concentrations they occupy a larger volume fraction.

Recently Abernethy et al. (1986) have presented and discussed data on LC50s for a variety of chemicals for Daphnia magna and Artemia and have successfully interpreted the results in terms of a postulated constant concentration of toxicant at the target site.

In this paper we discuss this issue further and present an analysis of these data and those of Veith et al. (1983) for fathead minnows and of K nemann (1981) for guppies. The aims are to shed some light on the mechanism of the narcotic effect, identify the relationship between LC50 and K_{OW} , suggest a method of including molar volume as a descriptor and suggest a novel correlation approach. It is emphasized that the thrust is to develop and discuss working hypotheses rather than prove their validity. The data analysis is unconventional, but it is hoped, revealing.

Hypothesis

We hypothesize that when the volume fraction of these chemicals in membranes reaches a critical value, narcosis occurs. Mullins (1954) suggested a figure of 1 to 3% and Carmichael (1985) a figure of approximately 1%. Apparently such "swollen" membranes are unable to function normally and narcosis results. The effect is usually reversible.

Assuming that the entire system of water-organism-target is at equilibrium we can state that the chemical's fugacity (f) in the water (W) and the target (T) site are equal. Applying the conventional (corrected Raoult's Law) equation (Prausnitz, 1969) gives

$$f_W = x_W \gamma_W f_R = f_T = x_T \gamma_T f_R \quad (1)$$

where x is mole fraction, γ is the activity coefficient and f_R is the reference fugacity or approximately the vapor pressure of the pure liquid chemical. It follows that

$$x_W \gamma_W = x_T \gamma_T \quad (2)$$

The group $x_W \gamma_W$ is the activity as discussed by Ferguson, thus if γ_T is constant for a series of chemicals, equal activity implies equal x_T or equal target site concentration. The volume fraction at the target site y is

$$y = x_T v_C / (x_T v_C + (1 - x_T) v_T) \quad (3)$$

where v_C is the molar volume of the chemical, v_T the molar volume of the target site material and $(1 - x_T)$ is the mole fraction of non-toxicant organic material at the target site. Since y for narcosis appears to be of the order of 0.01 it is apparent that $x_T v_C$ is much smaller than $(1 - x_T) v_T$ and that $(1 - x_T)$ is approximately unity, thus

$$y \approx x_T v_C / v_T \quad (4)$$

This definition of y is more equivalent to a volume ratio, than a volume fraction.

Combining equations 2 and 4 gives

$$y = x_W \gamma_W v_C / (v_T \gamma_T) \quad (5)$$

LC50 concentrations (C_W) are conveniently expressed in mol/m³, or an equivalent unit. Now C_W , is related to mole fraction for dilute solutions as

$$C_W = x_W/v_W \quad (6)$$

where v_W is the molar volume of water (18×10^{-6} m³/mol).

The term γ_W is the primary determinant of K_{OW} , the relationship being (Miller et al., 1985).

$$K_{OW} = C_O/C_W = x_O v_W / x_W v_O = \gamma_W v_W / \gamma_O v_O \quad (7)$$

where subscript O refers to octanol saturated with water.

Combining equations 6 and 7 with 5 gives

$$y = (C_W K_{OW} v_C) (\gamma_O v_O / \gamma_T v_T) \quad (8)$$

The first group of terms is entirely specific to the chemical and independent of the organism. The second is specific to the chemicals' behaviour in octanol and the target and is actually a target-octanol partition coefficient, which is believed to have a magnitude of approximately unity, but may vary depending on the nature of the chemical. We designate it as K_{TO} thus

$$y = C_W K_{OW} v_C K_{TO} \quad (9)$$

This equation can be viewed as simply

$$y = C_T v_C \quad (10)$$

where C_T is the target concentration (mol/m^3), with C_T being expressed as the product $C_W K_{TW}$, and K_{TW} the target water partition coefficient being further broken down as the product ($K_{OW} K_{TO}$).

If y and K_{TO} are constant, experimental values of the group $C_W \cdot K_{OW} \cdot v_C$ or $\text{LC50} \cdot K_{OW} \cdot v_C$ should be constant. If that group varies, it is interesting to explore whether the variation is related to variations in K_{OW} , C_W , or v_C . The obvious first step is to examine the magnitude of the group $C_W K_{OW} v_C$ or specifically $\text{LC50} \cdot K_{OW} \cdot v_C$.

It transpires that the group is remarkably constant, but contains some variation. We now hypothesize that y is actually constant, and we suggest later a technique for estimating its value. Experimental data are available to estimate the group ($C_W K_{OW} v_C$). The only remaining variable is K_{TO} which must contain the source of the variation, and which can then be determined and correlated, using an assumed constant value of y and the experimental data.

Data Analyses

QSAR data sets for fathead minnows (Veith et al., 1983), guppies (Könemann, 1981) and Daphnia and Artemia (Abernethy et al., 1985; 1986) have been analysed as follows.

The LC50 values were ranked in decreasing order for each data set and are listed in Table 1 for the two fish and two crustaceans. Different K_{OW} values for the same compounds between data sets were not adjusted and are shown as given by the original authors. Molar volume was calculated by the Le Bas method (Reid et al., 1977) recognizing that an error of up to a factor of 2 is possible, especially for the smaller molecules. The product of LC50 (mol/m^3), K_{OW} and molar volume v_C (cm^3/mol), divided by 10^6 to give units of m^3/m^3 , was

calculated for each data point. No distinction was made between chemical classes which include alcohols, ketones, ethers, alkanes, cycloalkanes, mono-aromatics, PNAs and a variety of chlorinated hydrocarbons. Nor was a distinction made between test species; all 153 data points being shown as one symbol ($n = 42$ for fathead minnows, $n = 38$ for guppies, $n = 39$ for Daphnia, $n = 34$ for Artemia). The strength of this data set lies in the number of data points which, it is hoped, is sufficient to enable broad trends to be identified despite differences in QSAR test systems. It is recognized that there are differing sensitivities between species, but if narcosis has a common mechanism, these differences should "average out". Later it may be appropriate to analyse smaller species-specific data sets and obtain more accurate species-specific correlations.

The results are presented in Table 1 and in Figures 1, 2 and 3 in which the ordinate is y/K_{TO} or $(LC50 \cdot K_{OW} v_C)$. It is striking that while $LC50$ and K_{OW} vary over 7 orders of magnitude and v_C by a factor of 3, the group y/K_{TO} varies only from 0.004 to 0.05, a factor of 12.5, for 90% of the chemicals in all four organisms.

There is a tendency for (y/K_{TO}) to increase with increasing K_{OW} and v_C and decrease with $LC50$. We hypothesize that this is due to a decrease in K_{TO} for substances of lower water solubility and hence higher K_{OW} , usually higher v_C , and lower $LC50$.

Eleven of the chemicals in Veith's data set, (mostly alcohols and ketones) have $\log K_{OW}$ values within the range of zero plus or minus 1.2 units. These chemicals show approximately equal affinities for aqueous and octanol phases and may also (we hypothesize) display equal affinities for the target phase. If this is accepted, K_{TO} for these chemicals is approximately unity

thus their mean value of (y/K_{TO}) equals the volume fraction y and is a "true" volume fraction. The mean value is 0.0063, i.e. $\log y$ is -2.2. We hypothesize that this is a universal volume fraction and that the variation in (y/K_{TO}) shown in Figures 1, 2 and 3 is entirely due to K_{TO} and, of course, experimental error. This enables us to develop a correlation for K_{TO} .

The $\log y$ versus $\log K_{OW}$ data were treated by first rejecting about 10% of the "outlying" points then drawing a straight line through the point at which $\log y$ is -2.2 and $\log K_{OW}$ is 0, such that it split the set of points into two approximately equal groups. The resulting slope on the log-log plot was approximately 0.14. It is thus suggested that

$$K_{TO} = K_{OW}^{-0.14} \quad (11)$$

Examination of the activity coefficient bases for K_{TO} and K_{OW} shows that

$$K_{TO} = (\gamma_O v_O / \gamma_T v_T) = (\gamma_W v_W / \gamma_O v_O)^{-0.14} \quad (12)$$

or

$$\gamma_T v_T = (\gamma_O v_O)^{0.86} (\gamma_W v_W)^{0.14} \quad (13)$$

or

$$\gamma_T \propto \gamma_O^{+0.86} \cdot \gamma_W^{+0.14} \quad (14)$$

Now correlations of K_{OW} versus solubility usually generate slopes of approximately -0.7 to -0.9 which Miller et al. (1985) have interpreted as being the combination of two factors. As γ_W increases (water solubility falls), K_{OW}

increases in proportion (i.e. $\propto \gamma_W^{+1.0}$) but γ_O also increases (i.e. the solubility in octanol falls) with an approximate relationship proportional to $\gamma_W^{0.1}$ to $\gamma_W^{0.3}$ thus the combined effect is a proportionality to the power of 0.7 to 0.9.

A convenient correlation of solubility and K_{OW} which was derived using many of the chemicals considered here is that of Chiou and Schemedding (1982) which is

$$\log K_{OW} = -0.862 \log S + 0.710 \quad (15)$$

where S is solubility in units of in mol/L. Converting to solubility C_S , or 1000 S mol/m³ gives the algebraically identical forms,

$$\log K_{OW} = -0.862 \log C_S + 3.296 \quad (16)$$

or

$$K_{OW} = 1977 C_S^{-0.862} \quad (17)$$

We interpret this as indicating that, since C_S is inversely proportional to γ_W ,

$$K_{OW} \propto \gamma_W / \gamma_O \propto \gamma_W / (\gamma_W^{0.138}) \propto \gamma_W^{0.862} \quad (18)$$

Substituting γ_O as proportional to $\gamma_W^{0.138}$ in equation 13 gives

$$\gamma_T \propto \gamma_W^{(0.86 \times 0.138 + 0.14)} \propto \gamma_W^{0.26} \quad (19)$$

The net effect of a decrease in water solubility by a factor of 10, i.e. an increase in γ_W by a factor of 10, is an increase in K_{OW} by a factor of 7.28 (reflecting factors of 10 increase in γ_W and 1.37 in γ_O), a decrease in K_{TO} by a factor of 1.32 caused by factor increases in γ_O of 1.37 and γ_T of 1.82.

The net result is that the target site appears to be more hydrophilic than octanol, i.e. as chemicals increase in hydrophobicity or γ_W , their "solubility" in the target site decreases faster than it does in octanol, i.e. γ_T increases faster than γ_O . It is thus necessary to use a higher concentration in the water to "drive" the chemical into the target site to achieve the required volume fraction of 0.63%.

Figure 4 is a plot of y or $LC50 K_{OW} \cdot v_C K_{TO} + 10^6$ or $LC50 K_{OW}^{0.86} v_C + 10^6$, (i.e. assuming K_{TO} is $K_{OW}^{-0.14}$) versus K_{OW} . The constancy around a mean of 0.63% is apparent.

DISCUSSION

Octanol is thus an adequate surrogate for the target site but this analysis suggests that it is a little too hydrophobic. An alcohol such as hexanol could be better. The primary variable which controls the QSAR is clearly γ_W which influences solubility in water directly and thus target-water and octanol-water partitioning. As molecular volume increases in a homologous series, γ_W increases rapidly, γ_T more slowly and γ_O even more slowly.

There are two further noteworthy implications.

First, when correlating LC50s versus molecular properties we suggest that in addition to the conventional log LC50 vs. log K_{OW} plot, the data be examined to test the constancy of the group $LC50 \cdot K_{OW} \cdot v_C + 10^6$. This should have a value of approximately 0.01. Greater constancy can probably be obtained for a group

$$LC50 K_{OW}^{(1-n)} v_C \text{ or } LC50 \cdot K_{OW} \cdot v_C / K_{OW}^n \quad (20)$$

where K_{OW}^{-n} is essentially K_{TO} , the target octanol partition coefficient. We suspect that n will have a value of 0.1 to 0.2. It may also be possible to correlate K_{TO} with variables such as water solubility, γ_W or chemical molar volume. Ultimately, it may be possible to correlate γ_T or more probably the group $\gamma_T v_T$ as a function of molecular properties. If this can be done it becomes possible to avoid using octanol as a surrogate organic phase because

$$y = LC50 \cdot K_{OW} \cdot v_C \cdot K_{TO} = LC50 \cdot K_{TW} \cdot v_C = LC50 \cdot (\gamma_W \cdot v_W / \gamma_T v_T) \cdot v_C \quad (21)$$

The properties of the organism and its target site are entirely described by the group $(\gamma_T v_T)$. Neither v_T or γ_T can be determined individually but their product can be determined, if a constant value of y is assumed. For the data set treated here a typical value of $\gamma_T v_T$ is 1000 cm³/mol.

Second, the equation relating y to LC50 has the interesting property that it predicts a toxicity "cut off", i.e. a point at which the LC50 equals the solubility and at lower solubilities, the chemical can not exert a toxic effect. Graphically, on a plot of log LC50 vs. log solubility, the correlation line crosses the 45° diagonal at low solubility (Abernethy et al., 1986). If we adopt the Chiou-Schmedding correlation between C_S and K_{OW} we can determine the point of cut off as follows

$$\begin{aligned} y &= LC50 \cdot K_{OW}^{0.86} \cdot v_C = LC50 (1977 \cdot C_S^{-0.862})^{0.86} \cdot v_C \\ &= 683 (LC50/C_S) \cdot C_S^{0.26} \cdot v_C \end{aligned} \quad (22)$$

But LC50 equals C_S at the cut off and y is 0.0063 thus

$$\begin{aligned} C_S^{0.26} &= 9.22 \times 10^{-6} / v_C & v_C \text{ in m}^3/\text{mol} \\ &= 9.22 / v_C & v_C \text{ in cm}^3/\text{mol} \end{aligned} \quad (23)$$

or

$$C_S = 9.22^{3.85} / v_C^{3.85} = 5179 / v_C^{3.85} \quad (24)$$

The cut off tends to occur with non polar molecules of v_C approximately

300 cm³/mol, thus C_S is approximately 1.5×10^{-6} mol/m³ or 4×10^{-4} g/m³ or 0.4 µg/L. Chemicals which have solubilities in the ppb range are thus predicted to lie close to the toxicity cut off. It is interesting that the power on v_C is so large. This corresponds to an apparent rapid fall in toxicity as the cut off is approached. This effect has been previously observed and expressed as a statement that in a series of chemicals, there appears to be a molecular weight or volume cut off beyond which the chemicals become biologically inactive.

This analysis suggests that as molar volume increases in a homologous series, a number of factors combine to give an impression of the rapid onset of biological inactivity. Typically a 10% or factor 1.1 increase in v_C eg. approximately from 285 to 315 cm³/mol causes

- (i) an increase in γ_W (and a corresponding decrease in water solubility) by a factor of 5 (Miller et al., 1985),
- (ii) an increase in γ_T (and a corresponding decrease in "solubility" at the target by a factor of $5^{0.26}$ or 1.52.
- (iii) an increase in volume occupied per molecule by a fraction of 1.1.

The last two factors combined decrease the ability of the chemical to occupy volume in the target by a factor of $1.52/1.1$ or 1.38, necessitating an increase in water concentration by this factor to compensate for the loss of affinity to the target. A lower water concentration is needed to exert the toxic effect by a factor of $5/1.38$ or 3.6. But since the solubility of the chemical is inversely proportional to γ_W , this solubility has fallen by a factor of 5. The required LC50 concentration thus moves closer to the solubility as both fall. Eventually, the required water concentration or LC50 reaches the solubility limit and a cut off occurs. The approach to the cut

off is very non-linear, a 10% increase in molar volume necessitating a 38% increase in activity or ratio of water concentration to solubility.

Another factor which may also contribute to an even more rapid cut off is the onset of chemical solidification, i.e when the melting point is reached. All the solubilities discussed here are liquid or subcooled liquid solubilities. As molecular weight and volume increase the melting point falls and approaches the test temperature. Below the melting point the chemical cannot form solutions as concentrated as the subcooled liquid value since it is constrained to a lower solid solubility by virtue of the accessibility of a lower energy crystalline form.

CONCLUSIONS

This analyses of narcosis data for a variety of chemicals for four aquatic organisms suggests that simple $\log LC_{50}$ vs. $\log K_{OW}$ correlations should be regarded as only a first step in interpretation. It appears that narcosis occurs at a fairly constant volume fraction increase in the target site of approximately 0.63%. The factors contributing to this level of partitioning have been discussed and it is postulated that the target-water partition coefficient differs from the octanol-water partition coefficient. As a series of chemicals increases in molar volume or hydrophobicity, their "solubility" in the target phase tends to decrease, i.e. the activity coefficient increases, until a point is reached at which the water concentration required to drive the toxicant into the target phase to achieve the required volume fraction equals the water solubility. Beyond this point, chemicals appear to be biologically inactive.

An obvious next stage is to treat each species separately and quantify differences in species sensitivities in terms of specific target-water or target-octanol partition coefficients. But it would be useful if the correlation techniques were identical such that inter-species comparisons can be made more easily.

It is hoped that this discussion will encourage other innovative correlation and interpretation approaches and thus contribute to a fuller understanding of the fundamental biology and chemistry underlying QSARs.

REFERENCES

- Abernethy, S., Charles, C., Mackay D. 1985. Development of predictive organic contaminant structure-property-toxicity relationships for aquatic organisms, p 333-356 In Proceedings of the Technology Transfer Conference, Toronto, Dec. 1985. Ontario Ministry of the Environment.
- Abernethy, S., Bobra, A.M., Shiu, W.Y., Wells, P.G., Mackay, D. 1986. Acute lethal toxicity of hydrocarbons and chlorinated hydrocarbons to two planktonic crustaceans: the key role of organism-water partitioning. *Aq. Toxicol.* 8:163-174.
- Carmichael, F.J. 1985. General anaesthetics. p.265-289. H. Kalant *et al.* [Eds.] Principles of Medical Pharmacology, University of Toronto Press, Toronto.
- Chiou, C.T., Schmedding, D.W., Manes, M. 1982. Partitioning of organic compounds in octanol-water systems. *Environ. Sci. Technol. J.* 16:4-10.
- Ferguson, J. 1939. Use of chemical potentials as indices of toxicity. *Proc. R. Soc. Lond. Ser. B.* 127:387-404.
- Könemann, H. 1981. Quantitative structure-activity relationships in fish toxicity studies. *Toxicol.* 19:209-221.
- Miller, M., Wasik, S.P., Huang, G.L., Shiu, W.Y., Mackay, D. 1985. Relationships between octanol-water partition coefficient and aqueous solubility. *Environ. Sci. and Technol. J.* 6:522-529.
- Mullins, L.J. 1954. Some physical mechanisms in narcosis. *Chem. Rev.* 54:289-323.
- Prausnitz, J.M. 1969. Molecular thermodynamics of fluid-phase equilibria, Prentice Hall, New Jersey.
- Reid, R.C., Prausnitz, J.M., Sherwood, T.K. 1977. The properties of gases and liquids, 3rd ed., p.58. McGraw-Hill, New York.
- Veith, R.C., Call, D.J., Brook, L.T. 1983. Structure-toxicity relationships for the fathead minnow. *Can. J. Fish Aq. Sci.* 40:743-748.

Table 1: Toxicological and physical-chemical data used to calculate volume fraction for non-specific effects on fish and crustaceans.

COMPOUND (data source)	y/K TO	LOG LC50 ₃ (mol/m ³)	LOG Kow	MOLAR VOLUME (cm ³ /mol)
(Veith, et al., 1983)				
Triethylene glycol	0.0057	2.67	-1.17	180.00
Acetone	0.0060	2.15	-0.24	74.00
2-Methyl-2,4-pentanediol	0.0028	1.96	-0.70	155.00
2-Butanone	0.0082	1.65	0.28	96.00
Tetrahydrofuran	0.0071	1.48	0.46	81.00
2-Methyl-1-propanol	0.0096	1.28	0.74	92.00
3-Pentanone	0.0145	1.25	0.84	118.00
3-Methyl-2-butanone	0.0049	1.00	0.62	118.00
t-Butylmethyl ether	0.0204	0.90	1.30	129.00
Cyclohexanol	0.0147	0.85	1.23	122.00
Cyclohexanone	0.0041	0.73	0.81	118.00
4-Methyl-2-pentanone	0.0126	0.70	1.25	141.00
2-Phenoxyethanol	0.0056	0.40	1.16	155.00
2,2,2-Trichloroethanol	0.0058	0.30	1.38	122.00
5-Methyl-2-hexanone	0.0139	0.14	1.79	163.00
Acetophenone	0.0086	0.13	1.66	140.00
1,2-Dichloroethane	0.0069	0.08	1.79	93.00
Diisopropyl ether	0.0049	-0.05	1.56	152.00
3,3-Dimethyl-2-butanone	0.0011	-0.06	0.94	141.00
1,1,2-Trichloroethane	0.0083	-0.21	2.07	115.00
1,1,2-Trichloroethylene	0.0095	-0.47	2.42	107.00
2-Hydroxy-4-methoxyacetophenone	0.0081	-0.48	2.14	177.00
Di-n-butyl ether	0.0592	-0.60	3.08	196.00
5-Nonanone	0.0453	-0.66	3.00	207.00
2-Octanone	0.0117	-0.66	2.46	185.00
1-Fluoro-4-nitrobenzene	0.0027	-0.70	-2.02	127.00
2,6-Dimethoxytoluene	0.0121	-0.87	2.67	192.00
1,1,2,2-Tetrachloroethane	0.0166	-0.92	3.01	135.00
Benzophenone	0.0413	-1.08	3.38	207.00
Tetrachloroethylene	0.0035	-1.09	2.53	128.00
2,4-Dichloroacetophenone	0.0118	-1.21	3.02	182.00
1,3-Dichlorobenzene	0.0174	-1.28	3.38	138.00
2-Decanone	0.0290	-1.44	3.54	230.00
Pentachloroethane	0.0247	-1.44	3.64	156.00
1,4-Dichlorobenzene	0.0089	-1.56	3.37	138.00
Dipentyl ether	0.0663	-1.70	4.16	230.00
3,4-Dichlorotoluene	0.0528	-1.74	4.22	175.00
1,2,4-Trichlorobenzene	0.0480	-1.80	4.28	159.00
2,3,4-Trichloroacetophenone	0.0097	-2.05	3.73	203.00
Hexachloroethane	0.0466	-2.20	4.62	177.00
1,2,3,4-Tetrachlorobenzene	0.0897	-2.29	4.99	179.00
α,α-2,6-tetrachlorotoluene	0.0157	-2.38	4.24	217.00

(Konemann, 1981)	y/K TO	LOG LC50 ₃ (mol/m ³)	LOG K _{ow}	MOLAR VOLUME (cm ³ /mol)
Acetone	0.0041	2.04	-0.30	74.00
Diethylether	0.0201	1.46	0.88	92.00
Dichloromethane	0.0080	0.54	1.51	71.00
1,1-Dichloroethane	0.0160	0.31	1.92	94.00
1,2-Dichloroethane	0.0058	0.03	1.76	94.00
1-Chlorobutane	0.0274	0.02	2.35	117.00
1,2-Dichloropropane	0.0172	0.01	2.16	116.00
1,1,1-Trichloroethane	0.0355	0.00	2.49	115.00
Chloroform	0.0082	-0.07	2.02	92.00
Benzene	0.0105	-0.09	2.13	96.00
Toluene	0.0340	-0.13	2.59	118.00
1,3-Dichloropropane	0.0044	-0.13	1.71	116.00
1,1,2-Trichloroethane	0.0195	-0.15	2.38	115.00
Tetrachloromethane	0.0318	-0.34	2.79	113.00
Trichloroethane	0.0076	-0.38	2.20	115.00
m-Xylene	0.0611	-0.45	3.09	140.00
o-Xylene	0.0570	-0.48	3.09	140.00
p-Xylene	0.0570	-0.48	3.09	140.00
1,2,3-Trichloropropane	0.0165	-0.55	2.63	137.00
1,1,2,2-Tetrachloroethane	0.0302	-0.66	3.01	135.00
Monochlorobenzene	0.0128	-0.77	2.81	117.00
3-Chlorotoluene	0.0410	-0.84	3.31	139.00
Tetrachloroethane	0.0129	-0.97	2.95	135.00
Pentachloroethane	0.0440	-1.13	3.58	156.00
1,3-Dichlorobenzene	0.0234	-1.30	3.53	138.00
4-Chlorotoluene	0.0133	-1.33	3.31	139.00
1,2-Dichlorobenzene	0.0186	-1.40	3.53	138.00
3,4-Dichlorotoluene	0.0528	-1.50	3.98	175.00
2,4-Dichlorotoluene	0.0482	-1.54	3.98	175.00
1,4-Dichlorobenzene	0.0126	-1.57	3.53	138.00
1,3,5-Trichlorobenzene	0.0459	-1.74	4.20	159.00
1,2,4-Trichlorobenzene	0.0332	-1.88	4.20	159.00
1,2,3-Trichlorobenzene	0.0325	-1.89	4.20	159.00
2,4,5-Trichlorotoluene	0.0827	-2.06	4.72	181.00
1,2,3,4-Tetrachlorobenzene	0.0579	-2.43	4.94	179.00
1,2,3,5-Tetrachlorobenzene	0.0579	-2.43	4.94	179.00
1,2,4,5-Tetrachlorobenzene	0.0220	-2.85	4.94	179.00
Pentachlorobenzene	0.0693	-3.15	5.69	200.00

(Abernethy, et al., 1986)

Dichloromethane	0.0037	0.20	1.51	71.00
Trichloromethane	0.0064	-0.18	2.02	92.00
1,1,1-Trichloroethane	0.0153	-0.37	2.49	115.00
Benzene	0.0052	-0.40	2.13	96.00
Carbon tetrachloride	0.0127	-0.74	2.79	113.00
Cyclopentane	0.0150	-0.82	3.00	100.00
Pentane	0.0312	-0.87	3.30	116.00
Toluene	0.0057	-0.90	2.59	118.00
m-Xylene	0.0154	-1.05	3.09	140.00
p-Xylene	0.0137	-1.10	3.09	140.00
Trichloroethylene	0.0017	-1.23	2.42	107.00
Chlorobenzene	0.0038	-1.29	2.80	117.00
1,3,5-Trimethylbenzene	0.0290	-1.30	3.55	163.00
Hexane	0.0369	-1.35	3.80	131.00
Cyclohexane	0.0145	-1.35	3.44	118.00
Naphthalene	0.0214	-1.43	3.59	148.00
1,3-Dichlorobenzene	0.0115	-1.48	3.40	138.00
o-Xylene	0.0052	-1.52	3.09	140.00
1,2,4-Trimethylbenzene	0.0175	-1.52	3.55	163.00
1,4-Dichlorobenzene	0.0083	-1.62	3.40	138.00
Ethylbenzene	0.0038	-1.70	3.13	140.00
1,2,4-Trichlorobenzene	0.0356	-1.75	4.10	159.00
1,2-Dichlorobenzene	0.0055	-1.80	3.40	138.00
Methyl cyclohexane	0.0154	-1.82	3.86	140.00
2-Methylnaphthalene	0.0132	-1.98	3.87	170.00
2-Chloronaphthalene	0.0173	-2.00	4.08	144.00
1-Methylnaphthalene	0.0126	-2.00	3.87	170.00
1,3,5-Trichlorobenzene	0.0174	-2.06	4.10	159.00
1,2,3-Trichlorobenzene	0.0159	-2.10	4.10	159.00
Biphenyl	0.0104	-2.15	3.90	185.00
1,2,3,4-Tetrachlorobenzene	0.0285	-2.30	4.50	180.00
1,2,3,5-tetrachlorobenzene	0.0227	-2.40	4.50	180.00
1,2,4,5-Tetramethylbenzene	0.0072	-2.46	4.05	185.00
Octane	0.0431	-2.48	4.90	164.00
Pentachlorobenzene	0.0240	-2.92	5.00	200.00
Phenanthrene	0.0066	-2.94	4.46	199.00
9-Methylanthracene	0.0186	-3.19	5.12	219.00
Pyrene	0.0076	-3.35	4.90	214.00
Decane	0.0229	-3.70	5.70	229.00

γ/K
 T_0

 LOG
 $LC50_3$
 (mol/m³)

 LOG
 K_{ow}

 MOLAR
 VOLUME
 (cm³/mol)

(Abernethy, et al., 1986)

Dichloromethane	0.0138	0.78	1.51	71.00
Benzene	0.0210	0.21	2.13	96.00
Trichloromethane	0.0139	0.16	2.02	92.00
Toluene	0.0296	-0.19	2.59	118.00
Chlorobenzene	0.0268	-0.44	2.80	117.00
Cyclopentane	0.0282	-0.55	3.00	100.00
p-Xylene	0.0395	-0.64	3.09	140.00
o-Xylene	0.0386	-0.65	3.09	140.00
Carbon tetrachloride	0.0139	-0.70	2.79	113.00
m-Xylene	0.0313	-0.74	3.09	140.00
Pentane	0.0381	-0.78	3.30	116.00
Ethylbenzene	0.0273	-0.84	3.13	140.00
1,3,5-Trimethylbenzene	0.0679	-0.93	3.55	163.00
Cumene	0.0541	-0.94	3.50	149.00
1,2-Dichlorobenzene	0.0355	-0.99	3.40	138.00
1,2,4-Trimethylbenzene	0.0578	-1.00	3.55	163.00
1,4-Dichlorobenzene	0.0324	-1.03	3.40	138.00
Cyclohexane	0.0277	-1.07	3.44	118.00
Naphthalene	0.0479	-1.08	3.59	148.00
1,3-Dichlorobenzene	0.0263	-1.12	3.40	138.00
Hexane	0.0337	-1.39	3.80	131.00
Methyl cyclohexane	0.0377	-1.43	3.86	140.00
2-Methylnaphthalene	0.0417	-1.48	3.87	170.00
Biphenyl	0.0378	-1.59	3.90	185.00
1-Methylnaphthalene	0.0224	-1.75	3.87	170.00
1,2,4-Trichlorobenzene	0.0356	-1.75	4.10	159.00
2-Chloronaphthalene	0.0245	-1.85	4.08	144.00
1,2,3-Trichlorobenzene	0.0258	-1.89	4.10	159.00
1-Chloronaphthalene	0.0194	-1.95	4.08	144.00
1,2,3,5-Tetrachlorobenzene	0.0422	-2.13	4.50	180.00
1,3,5-Trichlorobenzene	0.0105	-2.28	4.10	159.00
1,2,3,4-Tetrachlorobenzene	0.0285	-2.30	4.50	180.00
Phenanthrene	0.0218	-2.42	4.46	199.00
Octane	0.0452	-2.46	4.90	164.00

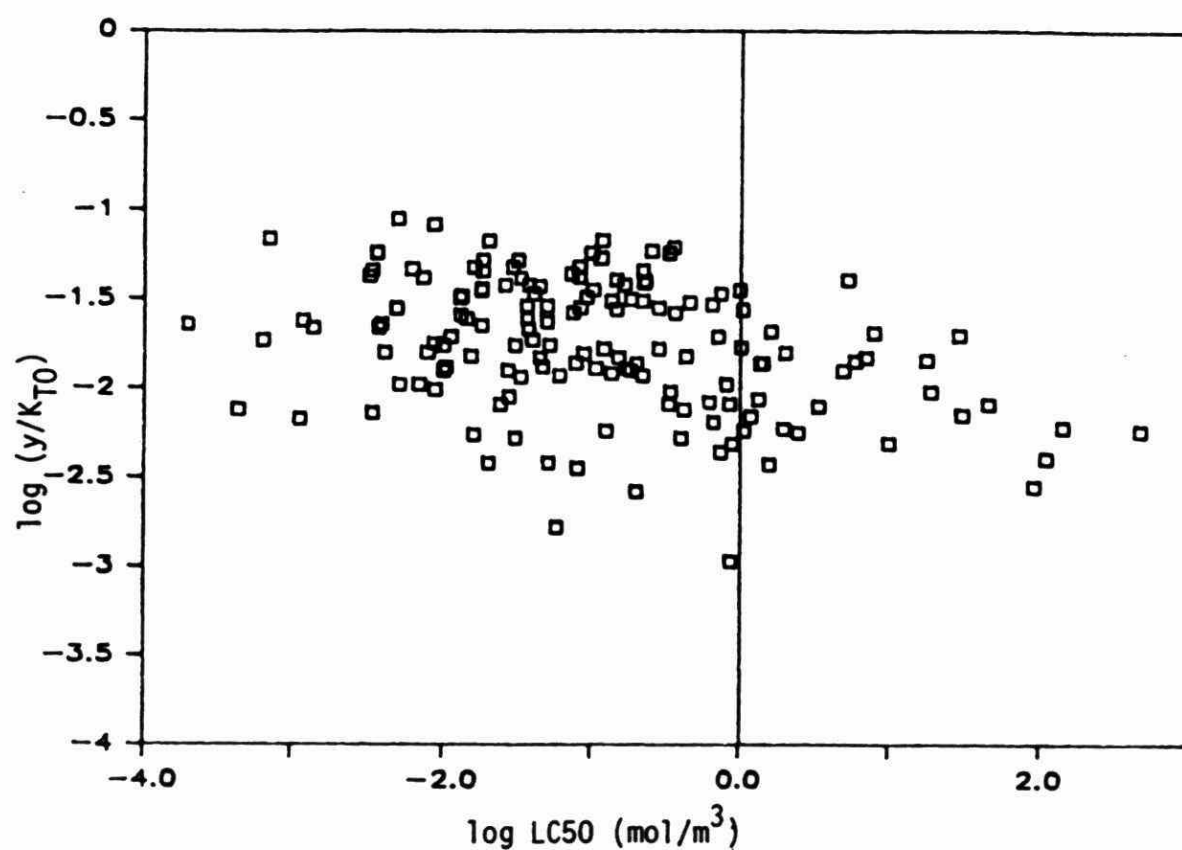


Figure 1: Variation in volume fraction as a function of median lethal concentration.

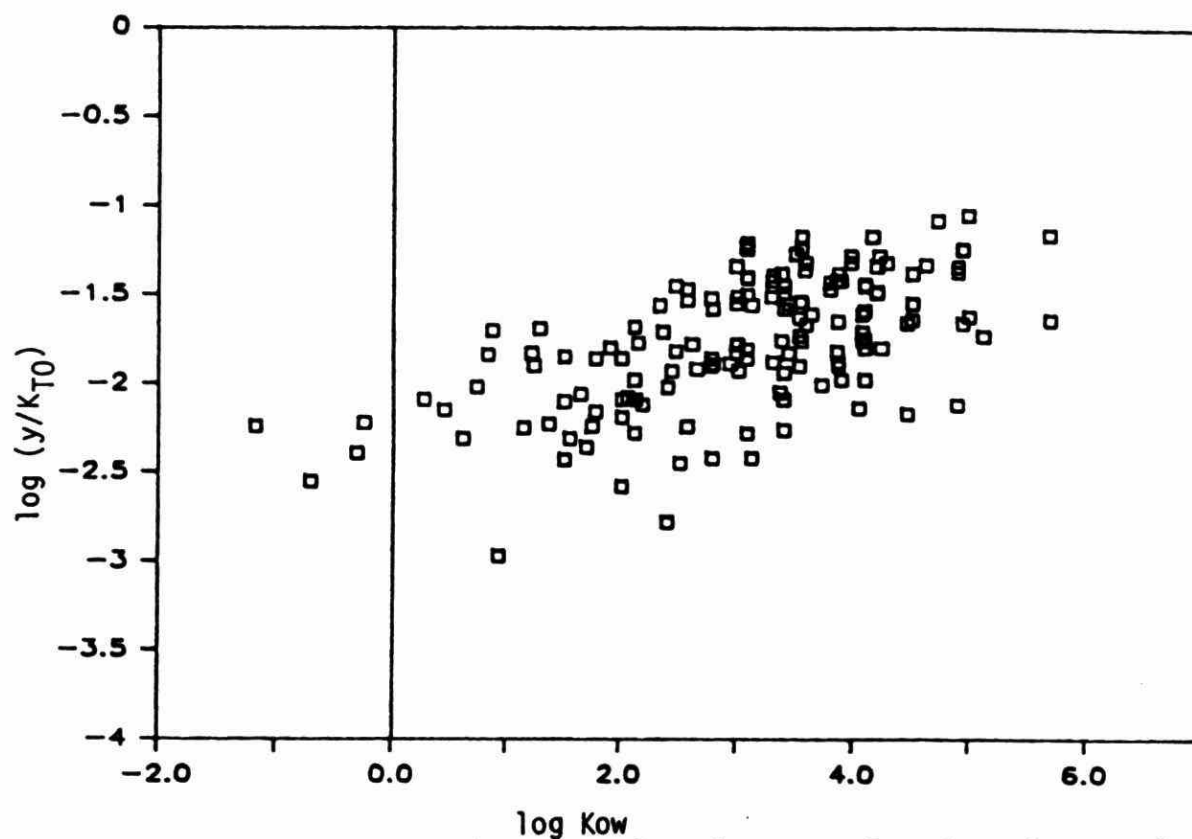


Figure 2: Variation in volume fraction as a function of octanol-water partition coefficient.

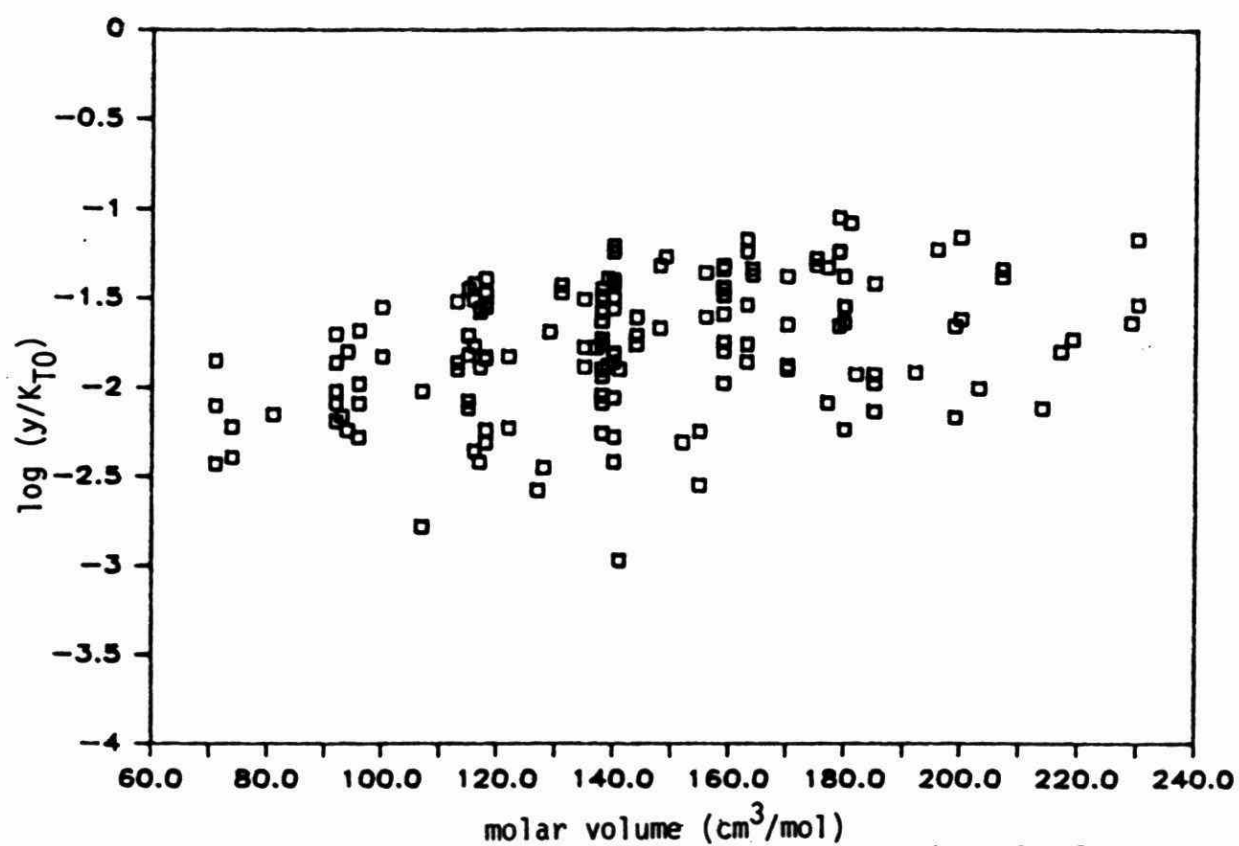


Figure 3: Variation in volume fraction as a function of molar volume.

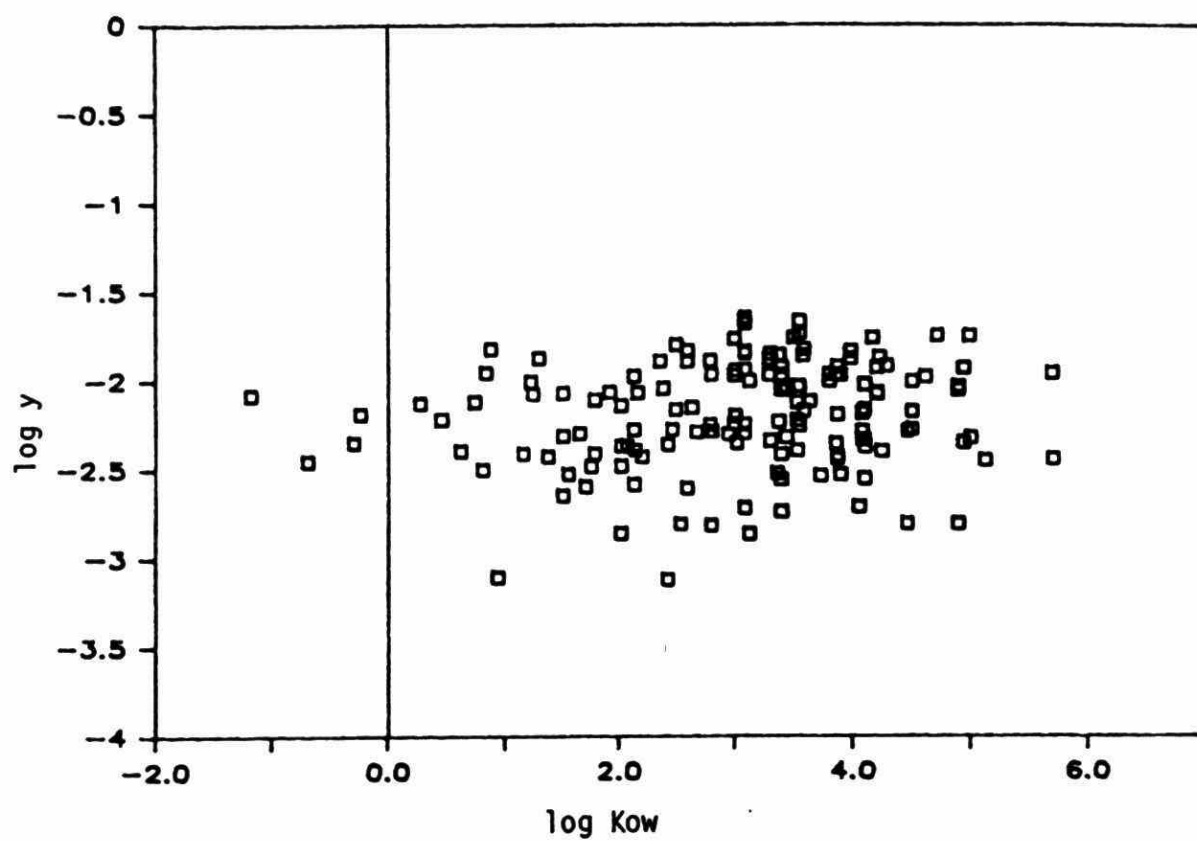


Figure 4: Variation in $y, (LC50 * K_{ow}^{0.86} * v \div 10^6)$ as a function of octanol-water partition coefficient.

EFFECT OF EXPOSURE TO LEAD, CADMIUM AND MERCURY
ON THE TISSUE OF FISH AND RATS:
DEVELOPMENT OF A BIOINDICATOR

NICHOLLS, D.M., Angelow, R. and Teichert-Kuliszewska, K.,
Department of Biology, York University,
North York, Ont. M3J 1P3

and

Girgis, G.R.,
Department of Applied Chemistry, Seneca College,
Finch Avenue, Willowdale, North York, Ont. M2J 2X5.

INTRODUCTION

There is considerable recent work which suggests that blood and tissue levels of environmental pollutants, such as the heavy metals, are not correlated with the functional impairment of the animal. Since protein synthesis is the broadest possible measure of overall animal health, it is surprising how few measurements have been carried out in animals growing in "healthy" environments,^{20, 21} let alone in environments polluted with cadmium, lead, and mercury. Protein synthesis in specific target tissues, such as muscle, liver, kidney and brain, have been studied in rats and more recently in fish in our laboratory.¹ The results indicate considerable pathology as the concentration of pollutant and time of exposure are increased.

In addition to studying the complex machinery of protein synthesis in these animals, we have focussed on simplifying the methodology by measuring the most crucial elements, namely mRNA and elongation enzymes.⁸⁻¹¹

Furthermore, there are several reports of heavy metal effects on several key metabolic enzymes of glycolysis and amino acid metabolism in fish exposed to relatively high levels of lead or cadmium.¹²⁻¹⁵ Thus, we have carried out a broad range of experiments in the laboratory on goldfish and field-collected yellow perch to examine some of these key metabolic enzymes, and additionally, membrane enzymes, since membranes are thought to be the primary site, for example, of mercury and methylmercury effects.

METHODS

Animals

Fish were 2-4 inches in size throughout the experiments. Goldfish (Carassius auratus) were exposed to dechlorinated Toronto tap water, ^{acidified to} pH 5.0, containing 5, 100 or 500 μg Pb/l as Pb acetate in a static bioassay for periods of 3, 6 or 20 weeks. The water (15 l) was acidified with an appropriate volume of H_2SO_4 added to the aquaria. In a subsequent series the acidified water contained 25 μg Pb/l in combination with 0.25 μg Cd/l and 0.25 μg Hg/l for 3 or 6 weeks. The next experiment used acidified water containing only Hg 30 μg /l for 3 weeks or 6 weeks. The fish were fed daily on fish pellets.

The aquaria were in a room at $17 \pm 1^\circ\text{C}$. The control water and metal-containing water were replaced weekly. In an experiment using 30 μg /l, the level of Hg detected in the water of the aquaria on the seventh day had fallen to approximately 1.5 μg /l. Normally each aquarium (15 l) contained no more than 10 fish.

A new series of experiments is studying rainbow trout (Salmo gairdneri) exposed in a flow bioassay system to Hg at concentrations of 0.2, 0.5, 1.0 and 5.0 μg /l for up to 2 weeks. Yellow perch from impacted and clean Muskoka lakes have been studied as well, either 1 or 2 days after collection.

Chemicals:

H_2SO_4 , HgCl_2 , $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$ and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$ were from Fisher Scientific Co., Don Mills, Ontario, and were of certified ACS grade. Other chemicals were obtained as described previously.

The components of the enzyme assays were obtained from Sigma Chemical Co., St. Louis, MO. U.S.A. L-[U-¹⁴C] leucine (339 Ci/mol) was from Amersham Corp., Oakville, Ontario.

Enzyme Assays:

Glyceraldehyde-3-phosphate dehydrogenase (GAPDH) EC 1.2.1.12 was assayed as described by Patnode et al. (1976)². Lactate dehydrogenase (LDH, EC 1.1.1.27) was assayed as described by Kornberg (1955)³ and aldolase (ALD, EC 4.1.2.13) was measured using a reagent kit obtained from the Sigma Chemical Co., St. Louis, MO, USA. Pyruvate kinase (PK, EC 2.7.1.40) was assayed as described by Bucher and Pfleiderer (1955)^{3a}. The method of Glossman and Neville (1972)⁴ was used to assay γ -glutamyltranspeptidase (EC 2.3.2.2) while alanine aminopeptidase was assayed by the method of Pfleiderer (1970)⁵. Alkaline phosphatase (EC 3.1.3.1) was as described by Quirk and Robinson (1972)⁶.

Preparation of tissue homogenates:

For muscle, the tissue was treated for 30 s in a mixer (model SDT: Tekmar, Cincinnati, OH, USA) before the homogenization step, while liver was homogenized directly. The tissues were homogenized in a glass homogenizer with 12-15 passes of a Teflon pestle in 1 mM EDTA and 1 mM 2-mercaptoethanol, pH 7.0, and centrifuged at 3000 x g for 20 min at 4°C as described by Patnode et al. (1976)². The resultant supernatant fluid was centrifuged at 10,000 x g for 20 min and the resultant clear supernatant fluid was frozen at -20°C or used immediately for determining the enzyme activities.

Protein synthesis:

Muscle and liver were homogenized as above in 3 volumes of buffer containing 0.25 M sucrose, 50 mM Tris.HCl (pH 7.8 at 24°C), 80 mM potassium acetate, 5 mM magnesium acetate, and 10 mM 2-mercaptoethanol. Centrifugation at 4°C at 15,000 g for 15 min and 105,000 g for 70 min to sediment the mitochondrial and microsomal fractions, respectively, yielded the postmicrosomal supernatant fraction (S105) as described by Sauvé and Nicholls (1981)⁹. The S105 fraction contained the enzymes of protein synthesis which were incubated with rat liver ribosomes as described by Sauvé and Nicholls (1981)⁹. The incorporation of [¹⁴C] leucine into protein was measured following termination of the incubation with 10% trichloroacetic acid and washing of the protein with hot 5% trichloroacetic acid. Solubilization of the protein for liquid scintillation counting was described previously (Sauvé and Nicholls, 1981)⁹. In other experiments ribosomes bearing mRNA were obtained from the microsomal fraction and were incubated with S105 supernatant fraction from rat liver (as a source of synthetases and elongation factors) as we described previously.¹⁰

Miscellaneous:

Protein concentration was determined according to the method of Lowry et al. (1951)⁷ using 1% bovine serum albumin as a standard. The RNA concentration was determined by the absorbance at 260 nm using A 1.0 = 50 g/ml. The absorbances were measured on a Zeiss model PMQII spectrophotometer. Values reported are

mean \pm SE. P-values by Student's t-test that are <0.05 are underlined.

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to lead for 3 weeks

	DOSE (μ g/l)	Enzyme Activity (μ moles/mg protein/hr)			
		LIVER		MUSCLE	
		Control	Lead	Control	Lead
Glyceraldehyde-3- phosphate dehydrogenase	500	12.6 \pm 1.2	13.2 \pm 0.6	11.4 \pm 0.6	6.6 \pm 0.6
	100	12.6 \pm 0.6	15.6 \pm 1.8	10.2 \pm 0.6	7.2 \pm 0.6
Lactate dehydrogenase	500	49.2 \pm 3.6	96.0 \pm 6.6	58.8 \pm 6.0	60.0 \pm 6.0
	100	48.0 \pm 3.6	82.2 \pm 9.0	57.6 \pm 10.8	56.4 \pm 3.6
γ -glutamyl transpeptidase	500	1.80 \pm 0.04	2.30 \pm 0.06		
	100	1.82 \pm 0.12	2.40 \pm 0.30		
Aminopeptidase	500	4.52 \pm 0.42	7.10 \pm 0.44		
	100	2.50 \pm 0.10	3.50 \pm 0.05		

Mean \pm S.D. for 2 experiments, each of 3-4 fish

TABLE 2

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to lead for 6 weeks

	DOSE ($\mu\text{g/l}$)	Enzyme Activity ($\mu\text{moles/mg protein/hr}$)			
		LIVER		MUSCLE	
		Control	Lead	Control	Lead
Glyceraldehyde-3-phosphate dehydrogenase	500	11.4 \pm 0.6	13.2 \pm 1.2	10.8 \pm 1.2	6.6 \pm 0.6
	100	12.0 \pm 1.2	14.4 \pm 1.2	10.2 \pm 0.6	8.4 \pm 0.6
Lactate dehydrogenase	500	54.6 \pm 1.2	115.2 \pm 12	60.0 \pm 4.8	66.6 \pm 4.8
	100	51.6 \pm 7.8	88.2 \pm 11	50.0 \pm 7.8	54.0 \pm 8.4
γ -glutamyl transpeptidase	500	1.60 \pm 0.07	2.46 \pm 0.36		
	100	1.49 \pm 0.27	1.81 \pm 0.26		
Amino-peptidase	500	3.65 \pm 0.20	7.78 \pm 0.15		
	100	4.17 \pm 0.27	6.25 \pm 0.41		

Mean \pm S.D. for 2 experiments, each of 3-4 fish

Table 3

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to low levels of mercury, cadmium and lead for 3 weeks.

Glycolytic Enzyme Activity
(μ moles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
Glyceraldehyde-3-phosphate dehydrogenase	13.2 \pm 0.42	11.4 \pm 0.42	16.8 \pm 0.60	10.2 \pm 0.62
Lactate dehydrogenase	38.4 \pm 3.6	45.0 \pm 6.0	46.2 \pm 5.4	20.4 \pm 0.60
Aldolase	7.60 \pm 0.24	7.22 \pm 0.90	44.0 \pm 3.0	40.7 \pm 1.7
Pyruvic kinase	63.5 \pm 2.3	61.4 \pm 0.89	98.3 \pm 6.6	100 \pm 4.3

Membrane Enzyme Activity
(μ moles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
γ -Glutamyl transpeptidase	1.48 \pm 0.06	1.61 \pm 0.07	0.89 \pm 0.17	0.67 \pm 0.16
Aminopeptidase	3.61 \pm 0.30	3.66 \pm 0.35	1.22 \pm 0.11	1.14 \pm 0.05
Alkaline phosphatase	7.89 \pm 0.55	10.1 \pm 0.34	11.8 \pm 0.46	9.83 \pm 1.06

Mean \pm SEM for 3 experiments of 6 fish.

The activity of enzymes of glycolysis and of membranes in fish tissue following exposure to low levels of mercury, cadmium and lead for 6 weeks.

Glycolytic Enzyme Activity
(μ moles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
Glyceraldehyde-3-phosphate dehydrogenase	11.6 \pm 0.72	10.9 \pm 0.60	12.6 \pm 0.60	<u>9.36</u> \pm 0.48
Lactate dehydrogenase	59.2 \pm 2.88	61.8 \pm 3.12	68.4 \pm 3.96	<u>51.9</u> \pm 1.50
Aldolase	8.97 \pm 0.34	8.31 \pm 0.22	40.4 \pm 2.13	43.0 \pm 1.58
Pyruvic kinase	62.8 \pm 1.86	60.0 \pm 0.65	96.3 \pm 4.85	99.2 \pm 4.24

Membrane Enzyme Activity
(μ moles/mg protein/hr)

	LIVER		MUSCLE	
	Control	Heavy Metals	Control	Heavy Metals
γ -glutamyl transpeptidase	1.61 \pm 0.12	1.84 \pm 0.05	1.04 \pm 0.09	1.11 \pm 0.08
Aminopeptidase	3.17 \pm 0.09	3.27 \pm 0.19	1.82 \pm 0.21	1.56 \pm 0.09
Alkaline phosphatase	7.59 \pm 0.81	<u>13.9</u> \pm 0.58	12.6 \pm 0.13	10.0 \pm 0.10

Mean \pm SEM for 3 experiments of 6 fish.

TABLE 5

The activity of enzymes of glycolysis and of membranes in fish tissues
following exposure to mercury (30 µg/l) for 3 weeks

	Enzyme Activity (µmoles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Mercury	Control	Mercury
Glyceraldehyde-3- phosphate dehydrogenase	10.2 ± 0.6	<u>7.8</u> ± 0.6	15.0 ± 0.6	<u>10.2</u> ± 0.6
Lactate dehydrogenase	53.4 ± 1.2	43.2 ± 3.6	42.0 ± 2.4	<u>37.8</u> ± 3.0
Aldolase	8.91 ± 0.60	8.80 ± 0.53	46.0 ± 1.7	45.0 ± 1.9
Pyruvic kinase	64.7 ± 2.1	66.7 ± 1.8	96.7 ± 1.6	99.9 ± 1.6
γ-glutamyl transpeptidase	1.66 ± 0.12	1.72 ± 0.07	0.90 ± 0.06	0.85 ± 0.17
Aminopeptidase	3.50 ± 0.15	3.54 ± 0.13	1.67 ± 0.08	1.62 ± 0.09
Alkaline phosphatase	10.4 ± 0.79	<u>12.8</u> ± 0.63	11.3 ± 0.6	10.7 ± 0.15
Mean ± SEM for 3 experiments of 6 fish				

TABLE 6

The activity of enzymes of glycolysis and of membranes in fish tissues
following exposure to mercury (30 µg/l) for 6 weeks

	Enzyme Activity (µmoles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Mercury	Control	Mercury
Glyceraldehyde-3- phosphate dehydrogenase	10.4 ± 0.6	<u>6.0</u> ± 0.6	13.8 ± 0.6	<u>10.5</u> ± 0.01
Lactate dehydrogenase	48.0 ± 0.6	<u>39.6</u> ± 1.2	41.4 ± 3.0	<u>31.2</u> ± 0.6
Aldolase	9.07 ± 0.14	8.13 ± 0.15	44.8 ± 1.7	41.4 ± 1.8
Pyruvic kinase	61.6 ± 1.4	62.6 ± 1.3	97.6 ± 1.16	94.9 ± 1.5
γ-glutamyl transpeptidase	1.65 ± 0.07	1.48 ± 0.14	0.93 ± 0.03	<u>0.78</u> ± 0.04
Aminopeptidase	3.22 ± 0.14	3.32 ± 0.10	1.46 ± 0.05	1.47 ± 0.06
Alkaline phosphatase	9.67 ± 0.40	<u>13.5</u> ± 0.68	9.09 ± 0.49	9.76 ± 0.38

Mean ± SEM for 3 experiments of 6 fish

TABLE 7

The activity of enzymes of glycolysis and of membranes in perch from
impacted lake compared to goldfish

	Enzyme Activity (μ moles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Impacted	Control	Impacted
Glyceraldehyde-3- phosphate dehydrogenase	10.3 \pm 0.2	<u>6.96</u> \pm 0.3	14.5 \pm 0.8	<u>11.8</u> \pm 0.3
Lactate dehydrogenase	51.2 \pm 3.6	<u>44.8</u> \pm 3.1	42.8 \pm 2.1	39.2 \pm 2.1
γ -glutamyl transpeptidase	1.81 \pm 0.09	1.72 \pm 0.06	0.91 \pm 0.09	0.96 \pm 0.09
Alkaline phosphatase	10.9 \pm 0.27	12.1 \pm 0.28	13.4 \pm 0.42	10.3 \pm 0.67

Mean \pm SEM for 3 experiments of 6 fish

TABLE 8

The activity of enzymes of glycolysis and of membranes in perch from
a clean lake compared to an impacted lake

	Enzyme Activity (μ moles/mg protein/hr)			
	LIVER		MUSCLE	
	Control	Impacted	Control	Impacted
Glyceraldehyde-3-phosphate dehydrogenase	10.5 \pm 0.3	<u>7.8</u> \pm 0.4	14.3 \pm 0.9	12.1 \pm 0.6
Lactate dehydrogenase	40.2 \pm 1.8	<u>34.2</u> \pm 2.4	46.8 \pm 1.2	46.2 \pm 6.6
γ -glutamyl transpeptidase	1.51 \pm 0.06	1.65 \pm 0.07	1.05 \pm 0.08	<u>0.87</u> \pm 0.02
Alkaline phosphatase	9.77 \pm 0.43	10.9 \pm 0.11	10.8 \pm 0.39	10.6 \pm 0.77
Mean \pm SEM for 3 fish				

TABLE 9

Hg levels (ppm) in fish
determined at Ontario Ministry of the Environment Laboratories

Table No.	3	4	5	6	7	8
	3 wk	6 wk	3 wk	6 wk		
Hg Conc.	<u>0.25 $\mu\text{g/l}$</u>		<u>30 $\mu\text{g/l}$</u>		Impacted Lake	Impacted Lake
Control Fish	0.01	0.02	0.03	0.02	0.02	0.07
Exposed Fish	0.03	0.04	2.9	8.0	0.16	0.16

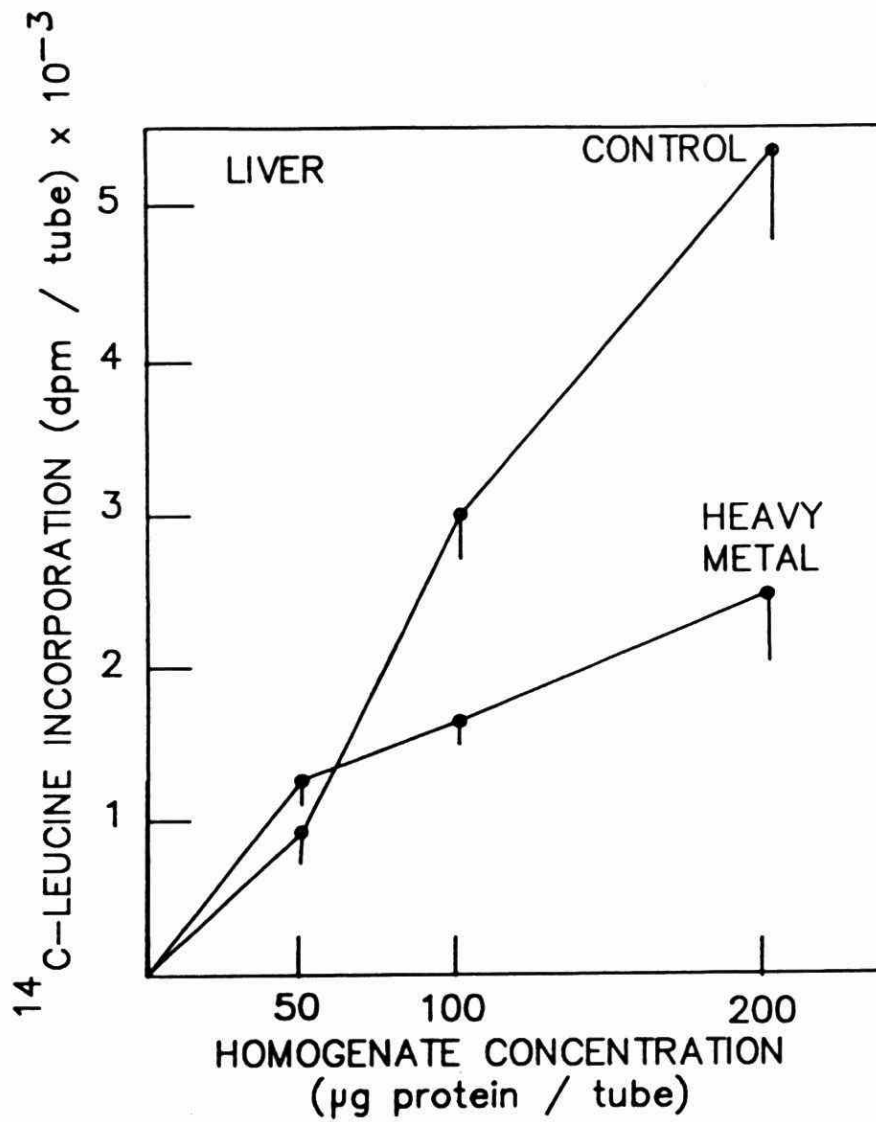


Fig. 1. Activity of soluble fraction of liver in protein synthesis in fish exposed to $0.25 \mu\text{g/l}$ Hg.

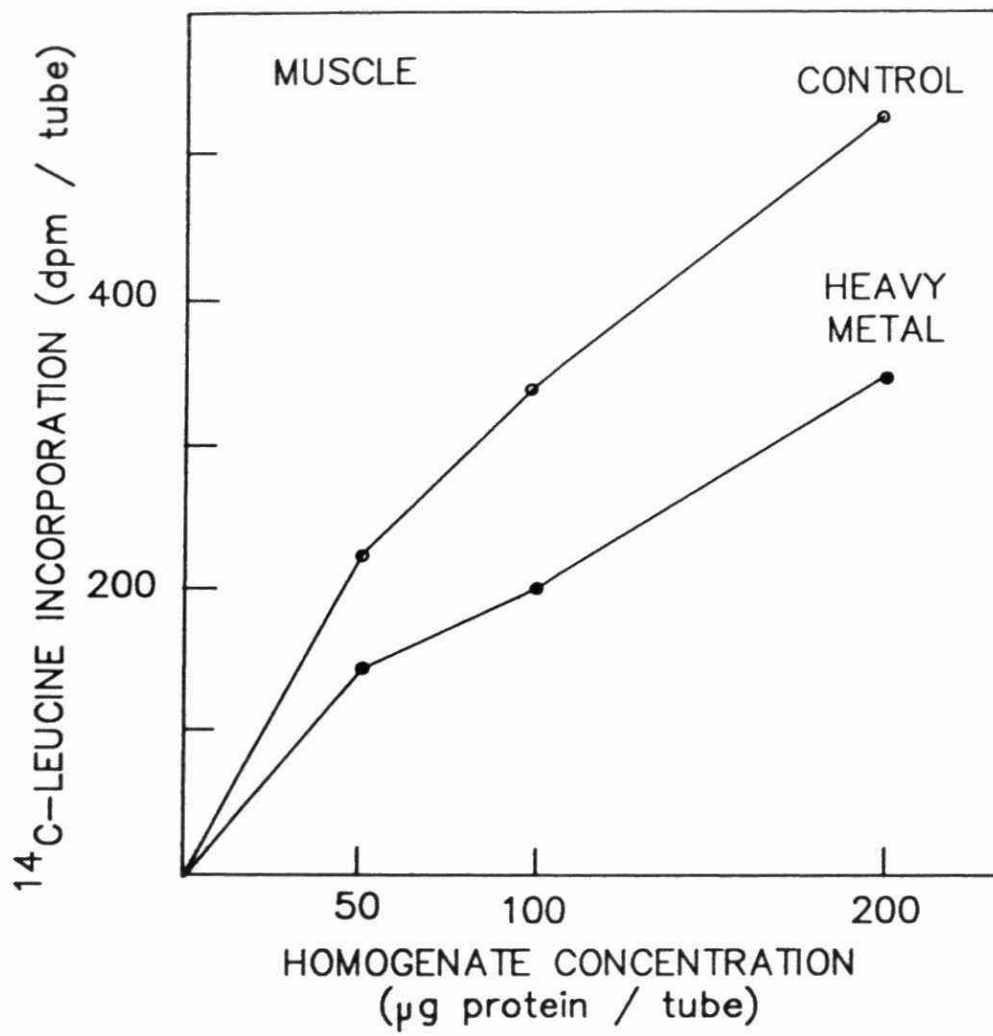


Fig. 2. Activity of soluble fraction of muscle in protein synthesis in fish exposed to $0.25 \mu\text{g/l}$ Hg.

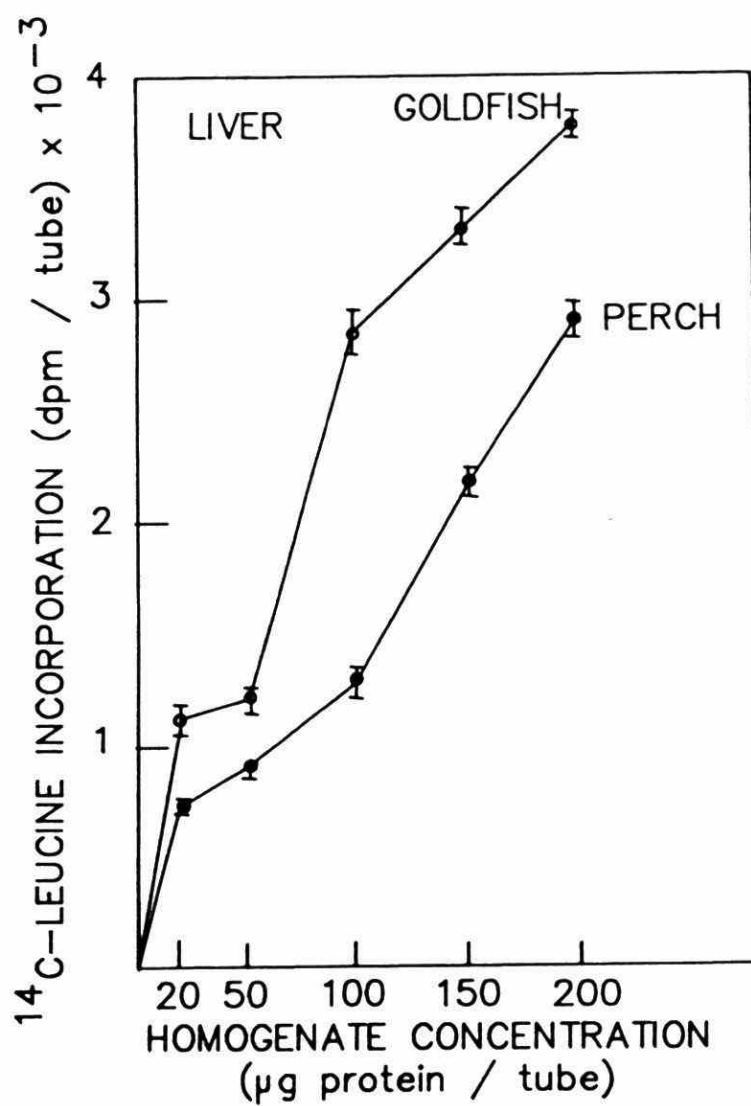


Fig. 3. Activity of soluble fraction of liver in protein synthesis in fish obtained from an impacted lake.

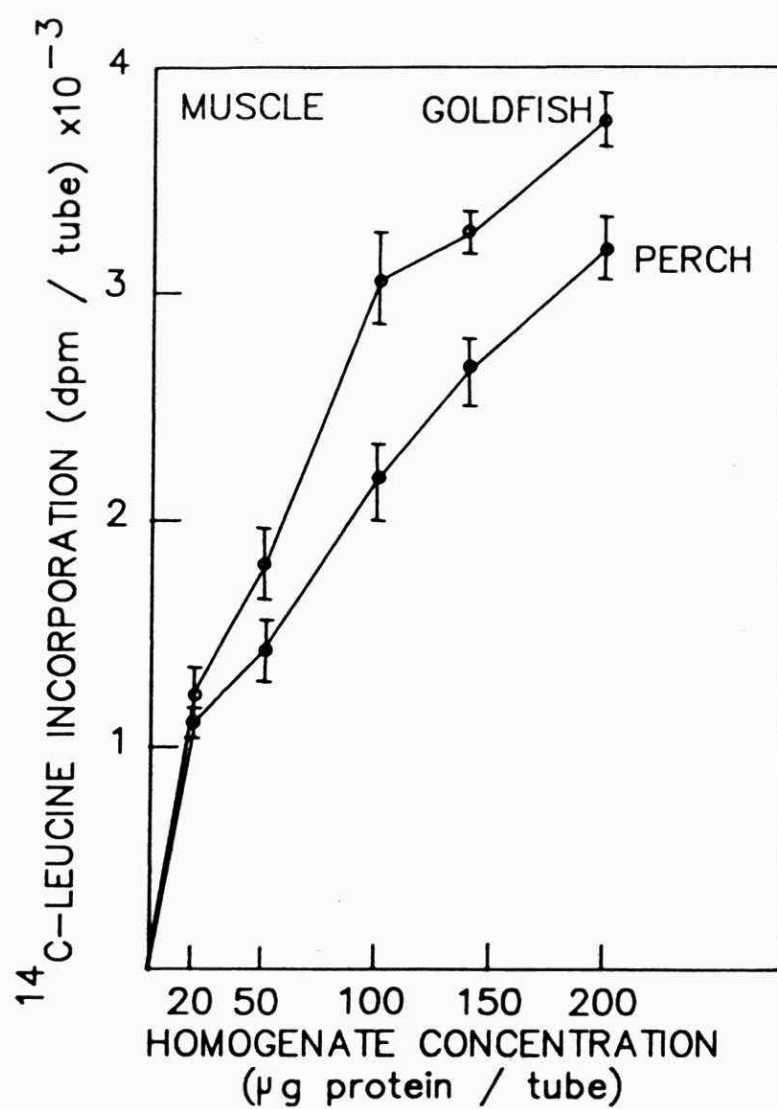


Fig. 4. Activity of soluble fraction of muscle in protein obtained in fish from an impacted lake.

Methylmercury induces α_1 -acid glycoprotein

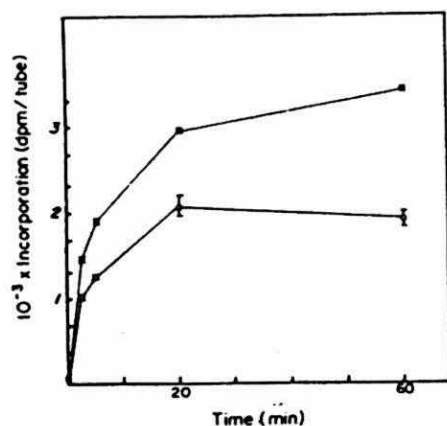


Fig. 2. The incorporation of [14 C]leucine into protein using polysomes from the liver of turpentine treated rats. Liver polysomes (250 μ g RNA/tube) were incubated with control liver postmicrosomal supernatant fraction (450 μ g protein/tube) at 37°C for varying times. The reaction mixture contained in a final volume of 0.4 ml the following: 50 mM Tris-HCl buffer (pH 7.7), 80 mM potassium acetate, 5 mM magnesium acetate, 20 mM 2-mercaptoethanol, 5 mM ATP, 0.5 mM GTP, 5 mM creatine phosphate, 50 μ g/tube creatine kinase and 0.25 μ Ci [14 C]leucine. The reaction was stopped with the addition of 3 ml 10% (w/v) trichloroacetic acid containing unlabelled carrier leucine and bovine serum albumin. The protein was heated at 90°C, washed and counted for radioactivity as described previously (Sauvé and Nicholls, 1981). Mean \pm SE. (○) Control; (●) turpentine

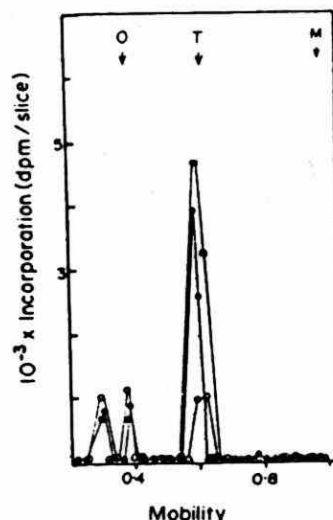


Fig. 3. SDS gel electrophoresis of liver proteins synthesized from [14 C]leucine in an mRNA-dependent reticulocyte lysate. Following incubation of 20 μ g RNA in the lysate mixture for 1 hr at 25°C, 20 μ l lysate was heated in sample buffer containing SDS and 2-mercaptoethanol and subjected to polyacrylamide gel electrophoresis. Control gels received 2050 dpm, "turpentine" gels received 3900 dpm and "methylmercury" gels received 4320 dpm. Markers were ovalbumin (O), trypsinogen (T) and metallothionein (M). (○) Control; (●) turpentine; (■) methylmercury.

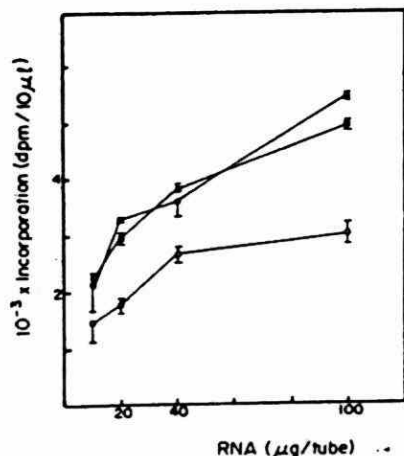


Fig. 4. The incorporation of [14 C]leucine into protein in an mRNA-dependent reticulocyte lysate using RNA preparations from liver of rats treated with turpentine or methylmercury. Incubation was as described in Materials and Methods in 50 μ l final volume. Mean \pm SE. (○) Control; (●) turpentine; (■) methylmercury.

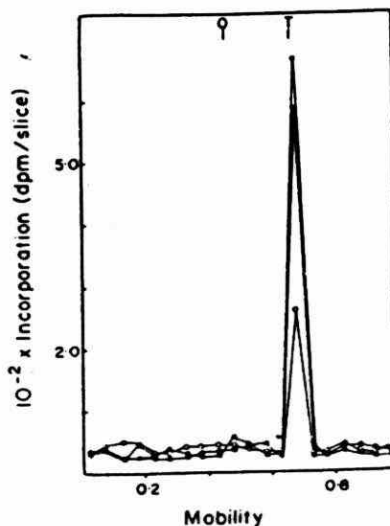


Fig. 5. Analysis of the mRNA translation product following immunoprecipitation with antiserum to α_1 -acid glycoprotein. The immunoprecipitates, prepared as described in Materials and Methods, were either counted or were placed in sample buffer for SDS polyacrylamide gel electrophoresis. Control gels received 2440 dpm, "turpentine" gels received 3800 dpm and "methylmercury" gels received 4800 dpm. Markers and symbols as in Fig. 3.

RESULTS

Liver and muscle enzymes:

These results are shown in Tables 1-8 and can be summarized as follows:-

Pb exposure of 100 or 500 $\mu\text{g/l}$ for 3 to 6 weeks resulted in statistically significant changes in the activities of liver lactate dehydrogenase and muscle glyceraldehyde-3-phosphate dehydrogenase, and liver membrane enzymes exhibited increased activities. Pb exposure of 5 $\mu\text{g/l}$ for 20 weeks exerted no effect on the enzyme activities. However, Pb exposures of 25 $\mu\text{g/l}$ for 6 weeks in combination with 0.25 $\mu\text{g/l}$ Hg and 0.25 $\mu\text{g/l}$ Cd resulted in significant decreases in the activities of muscle glycolytic enzymes and increases in liver membrane enzymes.

Similar changes in liver and muscle glycolytic and membrane enzymes were found in fish exposed for 3 or 6 weeks to 30 $\mu\text{g/l}$ Hg alone. An exception was that with Hg exposure, the activity of γ -glutamyl transpeptidase was decreased significantly in muscle though alkaline phosphatase activity was increased in the liver. Fish from the impacted lake exhibited a statistically significant decrease in the activity of glyceraldehyde-3-phosphate dehydrogenase and lactate dehydrogenase in liver tissue, while the membrane enzymes were very little affected.

Liver and muscle-protein synthesis:

These results are illustrated in Figs. 1-5 and can be summarized as follows:-

Fish exposed to Hg (0.25 $\mu\text{g/l}$) for six weeks exhibited statistically significant decreases in the enzymes of protein synthesis both in the liver, and also in the muscle, thus indicating an important reduction in the capability for growth. Fish from impacted lakes showed similar results.

In the continuous flow assay, low levels of Hg (e.g. 5.0 $\mu\text{g/l}$) trigger mRNA in fish liver for such activities as "acute phase" reactants¹⁷ and metallothioneins.¹⁸ These changes were analyzed by separating newly labelled proteins by polyacrylamide gel electrophoresis.

In experiments studying protein synthesis in young rats we have recently established that Cd and methylmercury exposure result in the stimulation of α_1 -acid glycoprotein, an "acute phase" reactant, believed to play a role in response to injury and/or inflammation.^{17,18} Further evidence for such a response in fish is currently being examined (Fig.5).

DISCUSSION

Our results for alkaline phosphatase activity in goldfish muscle and liver following low level Hg exposure, coupled with Cd and Pb, or following 30 $\mu\text{g Hg/l}$, are not in good agreement with recent observations of Sastry and Subhadra (1985)¹² who studied the effects upon freshwater catfish of exposure to high levels of Cd (260 $\mu\text{g/l}$) for 2-8 weeks. They noted decreased activity of alkaline phosphatase activity in liver as well as kidney and

intestine. In contrast, the activity in muscle was increased. Our results for 3 or 6 weeks Hg exposure show trends in the opposite direction.

Thus the changes we have observed in our experiments were marked ^{and} the identical trend found in goldfish was found in perch collected from an impacted lake.

By 8 weeks' exposure to this level of Cd, Sastry and Subhadra (1982)¹³ previously noted an inhibition in the activities of lactate dehydrogenase (and succinic dehydrogenase) in liver and muscle, in contradiction to changes after 2 or 4 weeks. Thus the results for goldfish after Hg exposure and Pb exposure for 3 or 6 weeks resemble the long term effect of Cd exposure which they reported. Most significantly, the observations of Sastry and Rao (1984)¹⁴ in the freshwater murrel exposed for long periods (17 weeks) to Hg (2.2 μ g Hg/l) included decreased activity of lactate dehydrogenase in liver and muscle. Our results for Hg and for Pb are also in accordance with acute sublethal exposures of killifish reported by Jackim et al. (1970)¹⁵.

In comparing Tables 3 and 4 with Figs. 1 and 2, it is clear that some statistically significant decreases in glycolytic enzymes could be detected but that the effect on the soluble machinery of protein synthesis was much more dramatic. Similarly, in comparing Tables 7 and 8 with Figs. 3 and 4, the effect on the soluble machinery of protein synthesis was much more dramatic than that on glycolytic and membrane enzymes. This is not so surprising when we remember that the soluble aminoacyl-tRNA

synthetases and the soluble elongation factors are very "fragile" enzymes and readily affected by interference with sulphhydryl groups in their structure. Thus, these proteins are prime targets for heavy metal effects.

The messenger RNA also is readily affected. It is induced by the "stress" of heavy metal exposure. Thus, the induction of metallothioneins and acute phase reactants in mammalian liver, and most likely in a wide range of fish, by heavy metal exposure is another type of genetic effect.^{8, 16-19} Our experiments with methyl-mercury show that rat liver DNA is stimulated, perhaps owing to a breakdown of membranes and consequent cell damage,¹⁸ to release more translatable messenger RNA coding for α_1 -acid glycoprotein.¹¹ Since this liver translation product is released to the blood, this acute phase reactant could be a useful indicator of heavy metal toxicity. In this regard, there is evidence that this protein is produced by Pb and Cd exposure, as well as methyl Hg exposure.

The paradox that the soluble protein synthesis machinery of the liver shows decreased activity while certain messenger RNA species show increased activity is seen in mammalian liver as well as in fish. It occurs as a result of the stimulation of the expression of specific genes, on the one hand, balanced by heavy metal suppression of the activity of the (sensitive) enzymes of the protein synthetic machinery, on the other hand.

Smith (1981)²⁰ proposed that the difference between fasted and fed synthesis rates measured in vivo in rainbow trout could be

used as a measurement of potential growth rate for species. The liver and gill synthetic rates were unaffected by 15 days starvation while muscle protein synthesis fell from 0.38% (of total muscle protein synthesized per day) to 0.09%, an 80% decrease. Since the growth of various fish species is reduced by exposure to Hg, Cd or other heavy metals, in laboratory controlled experiments, it is not surprising that we find decreased activity of muscle protein synthetic machinery as tested in vitro. This technique is much simpler than the in vivo measurements and, more importantly, groups of fish can be pooled, from collections from clean and impacted lakes, to give indications of growth impairment and of environmental pollution.

ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of K. Suns, Ontario Ministry of the Environment. The expert technical help of Andrea Miller, Susan Shepherd and Kathleen Lundy was much appreciated.

REFERENCES:

- 1 NICHOLLS, D.M., KULISZEWSKA, K., KULISZEWSKI, M.J. and GIRGIS, G.R. Canadian Congress of Biology, London, June 1985.
- 2 PATNODE, R., BARTLE, E., HILL, E.J. LEQUIRE, V. and PARK, J.H. (1976) J. Biol. Chem. 251: 4468-4475.
- 3 KORNBERG, A. (1955) Methods in Enzymology 1: 441-443.
- 3a BUCHER, T. and PFLEIDERER, G. (1955) Methods in Enzymology 1: 435-440.
- 4 GLOSSMAN, H., and NEVILLE, D.M. Jr. (1972) FEBS Lett. 19: 340-344.
- 5 PFLEIDERER, G. (1970) Methods in Enzymology 19: 514-521.
- 6 QUIRK, S.J. and ROBINSON, G.B. (1972) Biochem. J. 128: 1319-1328.
- 7 LOWRY, O.H., ROSEBROUGH, N.J., FARR, A.L. and RANDALL, R.J. (1951) J. Biol. Chem. 193: 265-275.
- 8 SAMJI, S., KULISZEWSKI, M.J., GIRGIS, G.R. and NICHOLLS, D.M. (1985) Can. J. Biochem. Cell Biol. 63: 913-918.
- 9 SAUVÉ, G.J. and NICHOLLS, D.M. (1981) Int. J. Biochem. 13: 981-990.
- 10 HARRISON, R.E. and NICHOLLS, D.M. (1985) Proc. Can. Fed. Biol. Soc. 28: 220.
- 11 HARRISON, R.E. and NICHOLLS, D.M. (1986) Comp. Biochem. Physiol. C. In Press.
- 12 SASTRY, K.V. and SUBHADRA, Km. (1985) Environ. Res. 36: 32-45.
- 13 SASTRY, K.V. and SUBHADRA, Km. (1982) Toxicol. Lett. 14: 45-55.
- 14 SASTRY, K.V. and RAO, D.R. (1984) Environ. Res. 34: 343-350.

- 15 JACKIM, E., HAMLIN, J. and SONIS, S. (1970). J. Fish. Res. Board Canada 27: 383-390.
- 16 ZAK, I. and DUBIN, A. (1978) Toxic. Appl. Pharmac. 46: 803-805.
- 17 KOJ, A. (1983) In: Pathophysiology of Plasma Protein Metabolism (ed. Mariani, G.) pp. 221-248, MacMillan, London.
- 18 DESNOYERS, P.A. and CHANG, L.W. (1975) Envir. Res. 9: 224-239.
- 19 ROCH, M. and McCARTER, J.A. (1986) Bull. Environ. Contam. Toxicol. 36: 168-175.
- 20 SMITH, M.A.K. (1981) J. Fish Biol. 19: 213-220.
- 21 FAUCONNEAU, B. and ARNAL, M. (1985) Comp. Biochem. Physiol. 82A: 179-187.

In situ assessment of mixed copper and zinc impacts on white sucker (Catostomus commersoni) populations in several Northern Ontario lakes.

K.R. Munkittrick and D.G. Dixon

Biology Dept., University of Waterloo, Waterloo, Ontario N2L 3G1

This project was undertaken as an integrated field-laboratory program designed to determine the impacts of copper and zinc contamination on white sucker (Catostomus commersoni) populations of several lakes in the Manitowadge district of Ontario. Lakes were evaluated on the basis of accessibility, preliminary sample collections and historical metal status. Manitowadge Lake (MAN) was selected as the lake with elevated levels of metals, Little Manitowadge Lake (LMN) was selected as the moderately contaminated site and Loken Lake (LOK) was selected as the control site (Figure 1). The lakes are very similar but differ in metal levels, most notably copper and zinc. Mean assayed copper concentrations (ug/l, std. dev., n.) were 15.3 for MAN (4.2, 35), 13.3 for LMN (3.7, 21) and less than 2.0 ug/l for LOK. Mean zinc concentrations (ug/l, std. dev., n.) were 253 for MAN (62.4, 35), 209 for LMN (20.3, 21) and 26.1 for LOK (22.4, 11).

Fish were collected by gillnet (3.5", 8.9 cm monofilament mesh) during the postspawning (POST) and recrudescence (RECR) periods during 1985 and 1986, and during the prespawning (PRES) and spawning (SPAW) periods of 1986. The gillnets were lifted every 40-60 min and the fish were sampled as soon as possible. The fish were weighed to the nearest 5 g and the standard length was recorded to the nearest 0.5 cm. Ages were estimated by pectoral ray sections, and fish older than 9 years were pooled.

Age, weight and length data for the metal contaminated sites were combined since there was no difference in the relationship of age with either weight ($p=.156$) or length ($p=.479$). At age 4 there were no significant differences in either length or weight between the control and metal sites (Figure 2), but control females were longer and heavier than metal fish at all ages older than 5. Results were similar for males (Figure 3).

Most of the individuals in these populations mature between 4 and 6 years of age, and contaminated fish are similar to control fish in length and weight until this age range. At LOK, 40.6 % (13/32) of the 4 and 5 year old female fish captured during PRES were immature and two 5 year old females captured during POST had failed to release their eggs. At MAN one 6 year old female, and two males of ages 5 and 7 were immature, while 6/19 (31.6%) females between the ages of 4 and 7 captured during POST had failed to release their eggs (two 4 year olds, one 5 and three 7). It appears that after attaining maturity, the metal contaminated fish are unable to meet the energetic requirements of both reproduction and growth. The increased impact on females supports this hypothesis since females require more energy for reproduction than males.

No effects of sex or season were found for condition factor ($k=100 \cdot wt/l^3$) ($p=.66, .29$), but condition factors of MAN fish (2.06, .02, 108) were significantly less than LOK (2.15, .02, 112; $p<.05$), although neither site was significantly different from LMN (2.11, .02, 129; $p>.05$). The increased k of LOK fish suggests that these fish put on proportionally more weight for increments in length.

Overall, the age of MAN fish (6.58, .18, 106) was not significantly different from LOK (6.34, .20, 110), although LMN fish were slightly older (7.13, .15, 125) ($p=.009$). The migrations of older fish at spawning times confounded the results of sex and site, and both MAN and LOK sites showed no effects of sex on age ($p=.54, .42$) and increases in the presence of males during the prespawning period (Table 1).

There were significant effects of sex, site and season on the hepatosomatic index (HSI). Female fish (mean, s.e., n; 1.51, .04, 86) had a larger liver than male fish (1.32, .04, 71; $p < .0001$). LOK fish had a smaller liver (1.28, .05, 46) than either MAN (1.43, .05, 50) or LMN fish (1.53, .05, 61) ($p = .0056$), and RECR fish had a smaller liver size (1.09, .05, 50) than either PRES (1.53, .03, 67) or POST fish (1.65, .05, 40) ($p < .0001$). Effects of metal contamination on liver size have been previously reported, although the significance awaits the completion of further analysis.

There was no effect of site on either male ($p = .299$) or female gonadosomatic index (GSI; $p = .355$) ($GSI = 100 \times \text{gonad wt} / \text{body wt}$) during maturation. As would be expected, there was a highly significant effect of season on both the male and female GSI ($p < .0001$). The large proportion of MAN females which failed to release their eggs can not be ignored and has been reported before for fish collected from metal contaminated lakes (McFarlane and Franzin, 1980). However, 2/30 control females also failed to spawn, and egg retention has been found in populations of white suckers from Lake Ontario (C. Portt, pers. comm.). The age of the fish which failed to spawn (mean = 5.5) suggests that these fish may have been attempting to spawn for the first time. Although the significance of this finding is not clear at this time, we can not attribute the result solely to the impact of metal contamination.

Control fish had significantly higher fecundity (31200, 2619, 19) than either MAN (22635, 746, 26) or LMN fish (21863, 958, 22) ($p < .0001$) at similar ages (LOK 7.0, 2.0, 20, MAN 6.9, 1.8, 26, LMN 7.3, 1.0, 24). Although, the fecundity of all fish showed highly significant positive relationships with length and weight, only LOK fish showed a positive relationship with age. Fecundity at both metal contaminated sites showed no relationship with age (Table 2) and is a reflection of the failure of these fish to show increases in weight or length after attaining sexual maturity. The inability of these fish to increase their fecundity with age could have serious consequences on the structure of the populations. Analysis of Lake Ontario samples is presently underway.

At spawning time, eggs were collected from individual females at each collection site, fertilized in duplicate with a pool of milt, water hardened and incubated in clean water before transportation to the University of Waterloo. For the first trials, control eggs were collected from a spawning site on Straight Lake (STR), a small lake adjacent to the Loken site. There was no significant difference in fertilization rate between MAN (79.7, 5.5, 20) and STR (82.2, 1.7, 20) ($p = .590$). Individual males were used to fertilize pools of eggs at each site and MAN estimates (87.7, 2.3, 20) were lower than STR (92.8, 0.8, 20) ($p = .019$), but identical trials using milt from LMN found the opposite to be true. Cross fertilization of LOK eggs with LMN milt yielded fertilization rates of 83.7% (3.3, 24) while the fertilization of the identical batch of eggs with LOK milt yielded lower rates (67.2, 1.8, 20; $p < .0001$). At the MAN site, enormous numbers of eggs were present on the stream beds, whereas few accumulations of eggs were present at the control site. It was not possible to collect large numbers of eggs from the control site redds so a pooled sample was necessary (156 eggs from 10 redds). There was no impairment of the fertilization process in gametes collected from the metal contaminated sites. The fertilization rates of eggs collected from 10 redds at MAN were 78.3% (7.6) while the fertilization rate of the pooled LOK sample was 78.0%.

The milt volumes of male suckers were significantly higher at both the MAN and LMN site than at either LOK or Lake Ontario collections ($p = .009$), but there was no difference in the concentration of sperm cells (spermocrit; $p = .672$). There was no effect of milt volume or sperm concentration on the fertilization rate using either LMN milt ($p = .17, .07$) or LOK milt ($p = .90, .35$).

MAN larvae were significantly shorter (10.48 mm, 0.10, 30; $p = .008$) and lighter (6.6 mg, 0.2, 30; $p = .011$) than the LOK larvae (10.85 mm, 0.12, 30; 7.3 mg, 0.3, 30) at 2 d post-hatch.

The rate of deformation was 3.78% for MAN and 2.50% for LOK. Eggs collected from the redds and hatched in the lab yielded a deformation rate of 6.0%. A "c" shaped deformity was predominant at the time of hatching, representing 100% of the LOK deformities, 82% of the MAN lab and 87% of the MAN redd deformities. Only 29% of deformities found in Lake Ontario suckers at the time of hatching were of this type. The significance of the higher deformation rate in situ demands further evaluation next year.

Although MAN larvae reached crucial developmental stages at times comparable to LOK larvae, the occurrence of swim bladder inflation, first feeding and yolk sac emptying occurred slightly earlier (Table 3). In addition to the slight increase in developmental rate, unfed MAN larvae died at a faster rate than LOK larvae (Figure 4). All MAN unfed larvae were dead by 29 d ph (post-hatch), while some LOK larvae continued to live until 42 d. Furthermore, an increase in the survival rate of MAN fed larvae over unfed could be detected by 25 d ph, while a similar point for LOK was 34 d ph.

Beginning at 1 d post-hatch (ph), larvae were exposed to waterborne copper in 144 hr continuous flow bioassays. New tests were started every 4 d until 37 d ph. Preliminary bioassays (1985-1986 report) found the 96 h LC50 to be around 350 ppb copper, and the survival times at 900 ppb to be less than 48 hrs. Lethal toxicity did not occur at these concentrations until 9 d ph, and it was necessary to add two additional concentrations (1200, 2200 ppb) at this time. Although it was not possible to calculate an accurate LC50 for MAN larvae at this age, LOK larvae showed higher mortality at 2200, 1200 and 900 ppb (Figure 5) (nominal: 144 hr LC50 1275 (1158-1402); 96 hr 886 (802-978)). Furthermore, the resistance times of MAN larvae to 2200 ppb copper was twice as long as LOK larvae (Figure 6). This suggests that the tolerance and resistance of MAN fish to copper was increased by a factor of at least 2 at this age.

The first mortalities for either larvae did not occur at the lower concentrations until after 9 d ph, the age at which blood is first thought to enter the gill arches (McElman and Balon, 1980). The differences in tolerance and resistance become less apparent as the fish aged and was not detectable at ages of 21 d ph. The food reserves of the larvae are decreasing over this time period, and the yolk sac appears empty at ages of 18-20 d ph. This time period corresponds to approximately halfway through the test started at 17 d ph, and before the test at 21 d ph. These tests show marked differences in both tolerance and resistance of the MAN larvae when compared with earlier tests (Figure 6).

Assays started at 29 d ph showed the resistance of fed fish to be higher than unfed at both sites (Table 4). This was the last day any MAN unfed larvae remained alive. Furthermore, all assays of MAN larvae started after the completion of yolk absorption (18-20 d) showed decreased resistance when compared with larvae tested before this time period (Table 5). If the increased tolerance and resistance of the MAN fish was the result of genetic adaptation, we would expect the increased survival to be evident at all ages tested. Bioassays conducted at 33 d, 37 d and 4 months of age do not show this to be the case. Furthermore, the LT50 at 2200 ppb copper for cross-fertilized larvae at 9 d ph (18.5 hrs, 17.2-19.5) was not significantly different from 9 d ph LOK unfed larvae (19.4 hrs, 17.6-21.4), and neither was the mortality rate at 900 ppb (3/10 at 9 d ph). In both cases these resistance times are significantly lower from the larvae from contaminated eggs and milt (9 d fed 44.8 hrs, 42.0-48.0, 9 d unfed 38.4, 36.0-41.0). In fact, the only time periods tested which suggest increases in tolerance and resistance are those conducted during the period of endogenous (yolk) nutrition, suggesting the presence of factors in the yolk which infer an advantage to survival. These factors appear to be maternal in origin and future trials will attempt to identify them.

This study is ongoing, and future research will concentrate on several areas. Body energy stores, tissue metal levels, metal-binding proteins and histological examinations of several species

of fish are currently underway. Future collections will involve the examination of several phenomena in more detail.

1) Weight-age relationships: the decreased length, weight, condition factors, fecundity, egg weight, larval size, larval survival and increased larval developmental rate of MAN fish are all consistent with the presence of decreased or impaired energy stores. Recent analysis confirms lower glycogen stores in the livers of metal contaminated fish during the autumn period of gonadal growth. Additional samples are needed to examine the energy and nutritional balance of the fish.

2) Deformity of larval suckers: The increased milt volume, altered egg density, and decreased egg size in MAN streams (when compared with lab studies) are suggestive of osmoregulatory abnormalities. Examination of the blood ion balance of the fish is currently underway, but it would be valuable to examine the consequences of the further decrease in egg size noted during in situ incubation on the size of the larvae after hatch. Additionally, the increased deformity rate in MAN streams (with respect to lab incubations) should be investigated further.

3) Increased larval tolerance: The increased resistance and tolerance of the MAN larvae appears to be related to a maternal factor present in the yolk. There is a need to examine this phenomenon further through a closer examination of the larval tolerance at the critical period of development (9d -20d ph), including more detailed cross-fertilization experiments.

Acknowledgements

This project was funded through the Ontario Ministry of the Environment (Project 193 R). Our appreciation is extended to Dr. C. Neville for her assistance during the course of this research. Additional financial assistance was received from the Natural Sciences and Engineering Research Council.

References

- McElman, J.F. and Balon, E.K. 1980. Env. Bio. Fish 5:191-224.
- McFarlane, G.A. and Franzin, W.G. 1980. J. Fish. Res. Bd. Can. 35:963-970.

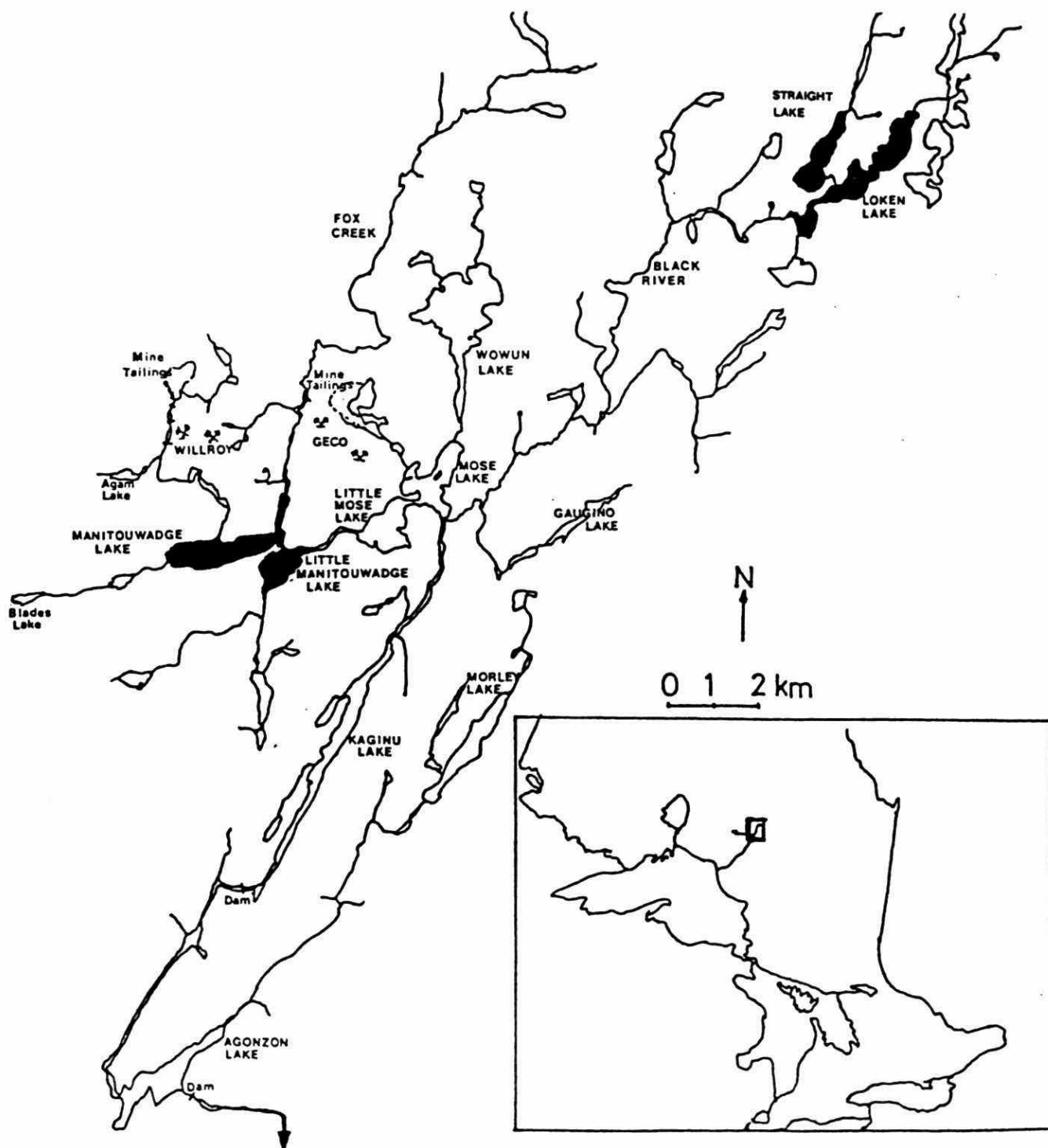


Figure 1. Map of the study site. Manitouwadge Lake represents the elevated metal site, Little Manitouwadge Lake the low metal site and Loken Lake the control site. Water flow is toward the south.

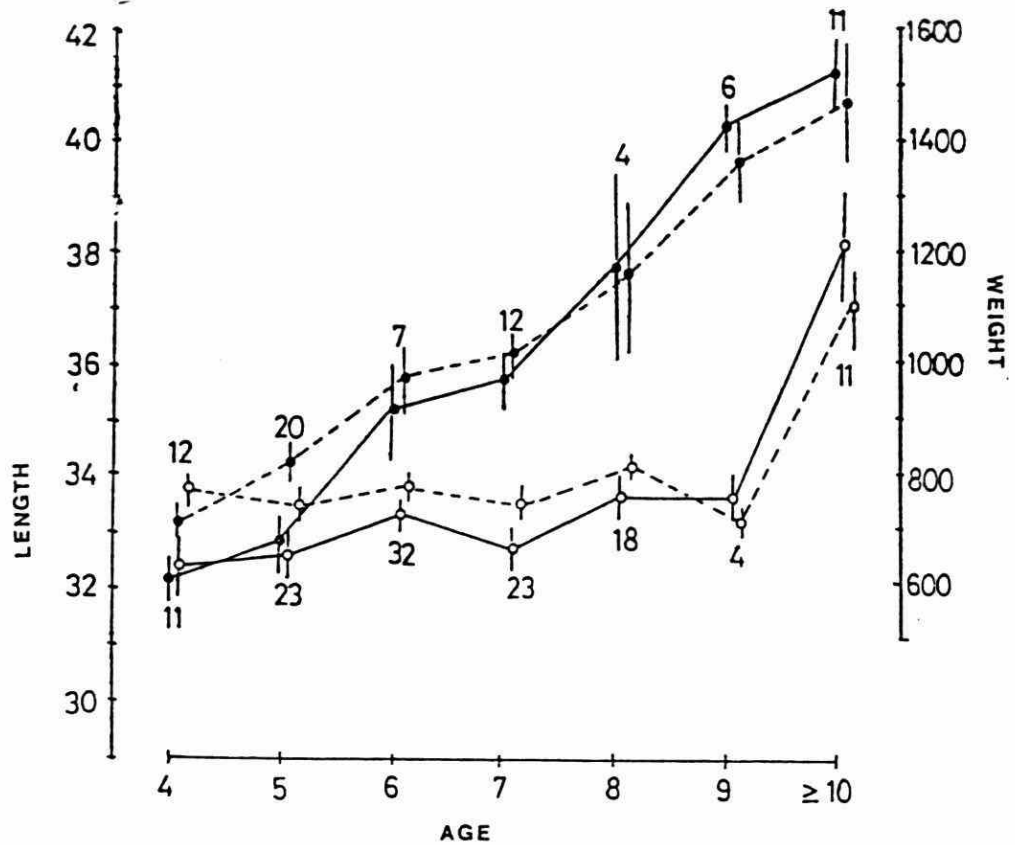


Figure 2. Weight (dotted line) and length (solid line) of female white suckers from the control site (closed circles) and metal sites (open circles). Values represent the mean \pm s.e. with the sample size shown.

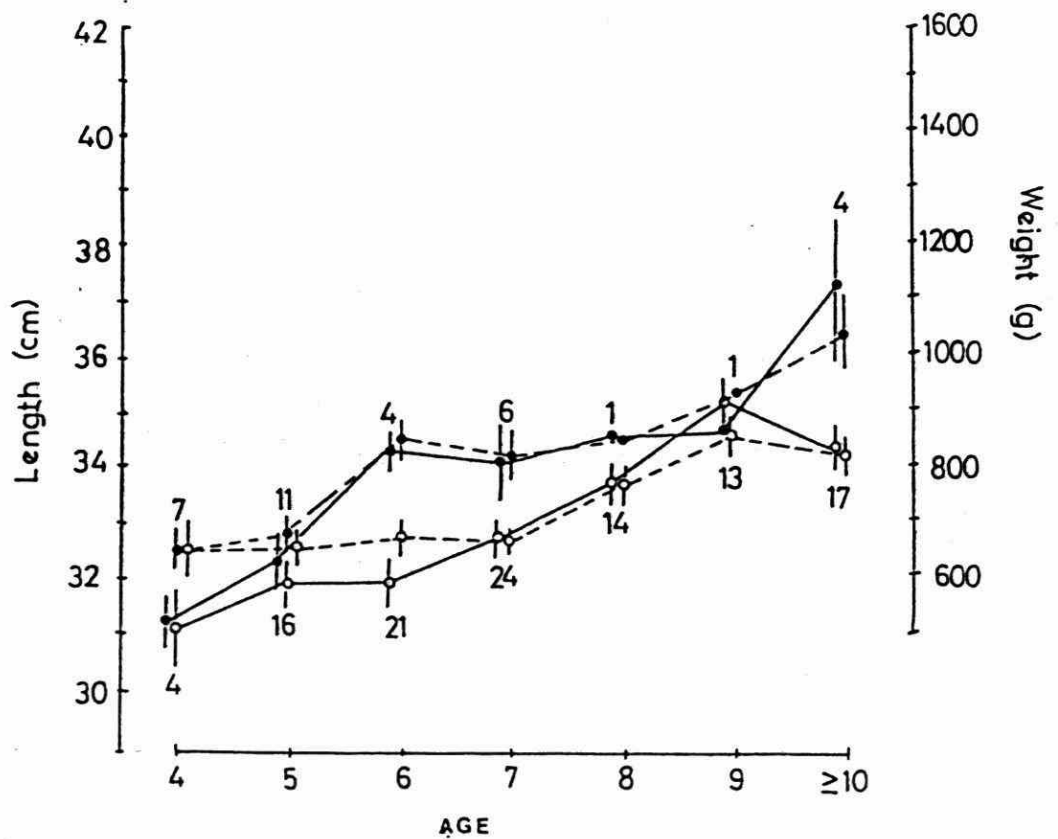


Figure 3. Weight (dotted line) and length (solid line) of male white suckers from the control site (closed circles) and metal sites (open circles). Values represent the mean \pm s.e. with the sample size shown.

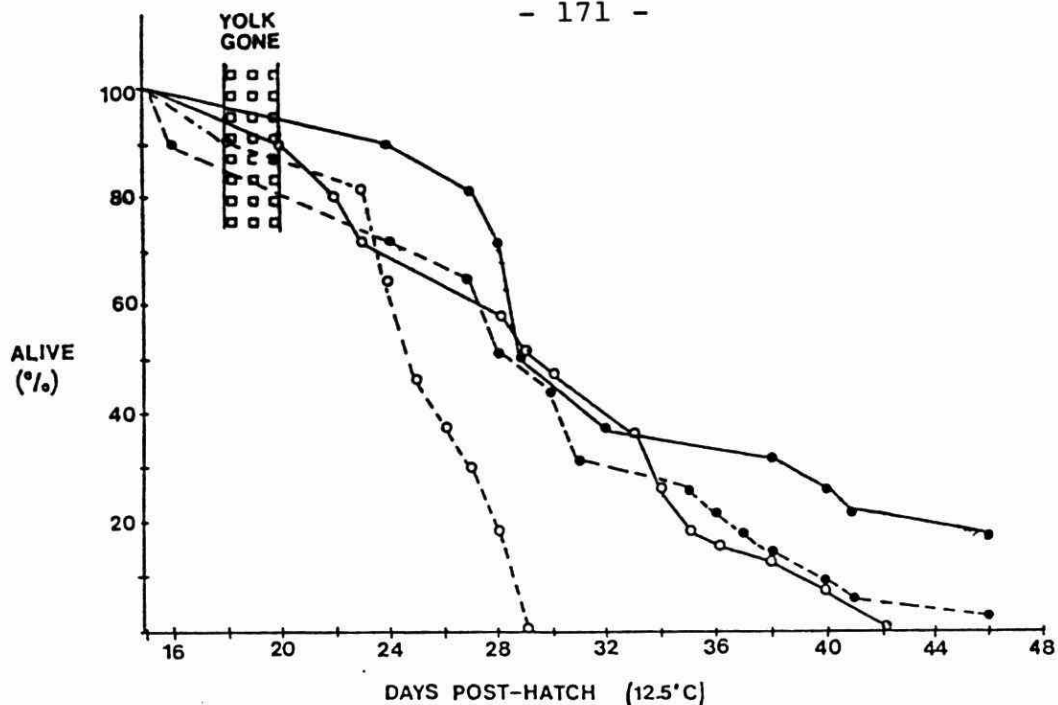


Figure 4. Survival of fed (closed circles) and unfed (open circles) white sucker larvae from the control site (LOK, solid line) and the metal contaminated site (MAN, dotted line). Deaths were calculated from the survival of bioassay control fish and survival was extrapolated from cumulative percent death.

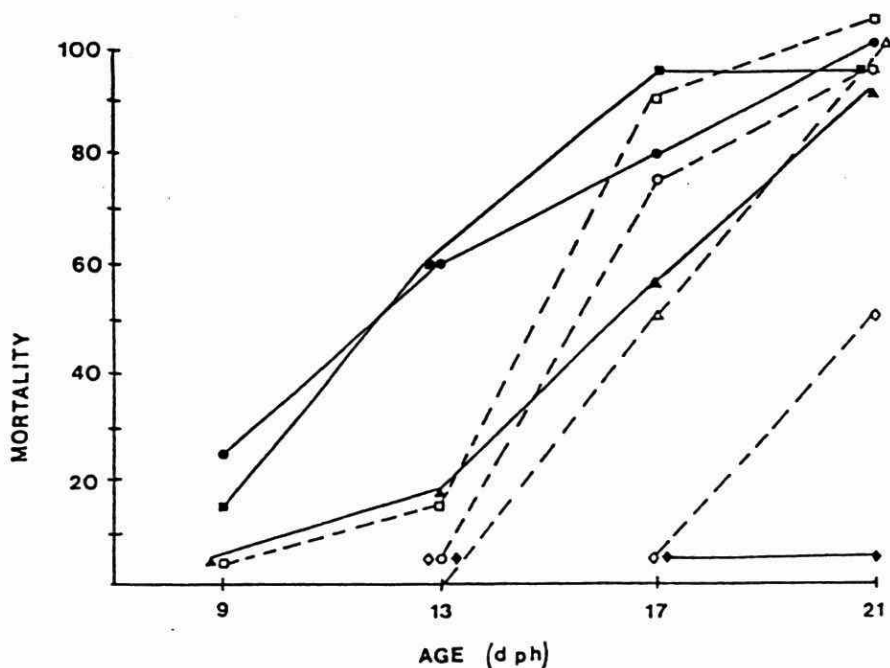


Figure 5. Survival of control (closed symbols) and metal contaminated (open symbols) white sucker larvae after 144 hr exposure to 1200 ppb (circles), 900 ppb (squares) and 600 ppb (triangles) of waterborne copper. Results show combined mortality of fed and unfed larvae ($n=20$) and diamonds represent control mortality. Age is represented by the age (d) at the start of the bioassay.

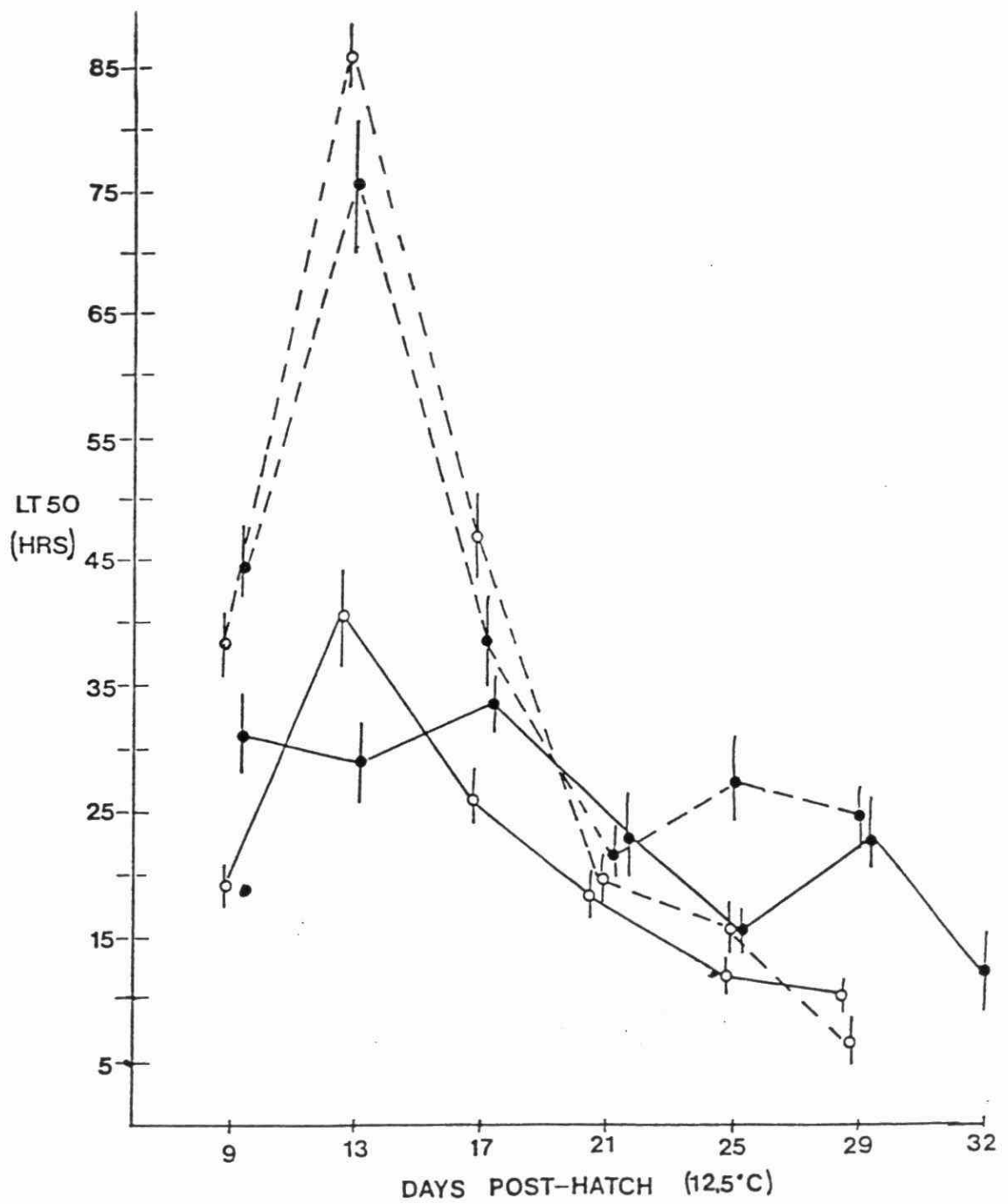


Figure 6. Resistance of white sucker larvae to 2200 ppb of waterborne copper. The time to 50% mortality (hrs) is given for fed (closed circles) and unfed (open circles) larvae from the control site (solid line) and the metal contaminated site (dotted line) at different ages post-hatch. Values are given with their 95% confidence intervals.

Table 1 Ages of white suckers collected from the control site (LOK) and metal contaminated sites. Values are expressed as mean \pm s.e. (n), those sharing a superscript are not significantly different (Tukey-Kramer test, $p > .05$) from other values for that size.

		Prespawning	Postspawning	Recrudescence
MAN	male	7.6 \pm 0.3 (23) ^a	6.1 \pm 0.3 (13) ^b	6.3 \pm 0.8 (8) ^b
	female	7.4 \pm 0.4 (19) ^a	6.0 \pm 0.4 (22) ^b	5.3 \pm 0.4 (21) ^b
LMN	male	7.5 \pm 0.3 (20) ^b	7.7 \pm 0.3 (28) ^a	7.1 \pm 0.3 (17) ^b
	female	7.2 \pm 0.2 (26) ^b	6.9 \pm 0.4 (22) ^a	5.5 \pm 0.4 (12) ^b
LOK	male	6.0 \pm 0.4 (19) ^a	7.7 \pm 0.7 (9) ^a	4.5 \pm 0.4 (8) ^c
	female	6.2 \pm 0.4 (25) ^b	7.0 \pm 0.3 (29) ^b	6.0 \pm 0.5 (20) ^b

Table 2. Coefficients for relationships of fecundity (total # eggs) with age, length and weight of control fish (LOK) and fish from metal contaminated sites.

	n	Slope	Intercept	R	R ²	p(Bo = 0)	p(Linear)
<u>Age (yr)</u>							
LOK	19	4602.4	-47.7	0.81	.860	.0001	<.001
LMN	22	1183.8	13310	0.27	.072	.226	
MAN	25	741.8	17613	0.34	.118	.093	
<u>Length (cm)</u>							
LOK	19	2259.0	-49708	0.94	0.990	.0001	<.001
LMN	22	1526.9	-29565	0.70	0.489	.0003	<.001
MAN	25	1092.4	-13602	0.83	0.399	.0005	<.001
<u>Weight (g)</u>							
LOK	19	25.92	3454	0.97	0.951	.0001	<.001
LMN	22	20.88	4679	0.80	0.641	.0001	<.001
MAN	25	22.68	5219	0.71	0.510	.0001	<.001

Table 3. Age at which white sucker larvae reach crucial developmental stages from the control (LOK) and MAN. Times are given in days post-hatch and daily temperature units (DTU). The developmental temperature was 12°C, and values are compared with published developmental times (McElman & Balon, 1980: assumes hatch at 5.5 d post-fertilization, developmental temperature was 15°C).

Critical Stage (McElman & Balon, 1980)		DTU	Predicted (12°C)	Days	MAN DTU	% exhibiting	LOK days	DTU	% exhibiting
I.	first swimming ($< 2.5\text{cm}$)	60	5	5	60		5	60	
II.	bile in gall bladder gill circulation complete	90	7.5	7	84		7	84	
III.	Mouth opening and closing pectoral fins moving, blood into gill arches	120	10	9	108		9	108	
IV.	Swim bladder inflated	150	12.5	9 11 12	108 132 144	30 90 100	10 12 13	120 144 156	5 50 100
V.	peristalsis, first food, first feces	165	13.8	18 21	216 252	20 100	20 22	240 264	20 100
VI.	Yolk gone	225	18.8	18-20	196-204		20	204	

Table 4. Time to 50% mortality (LT50) of white suckers larval exposed to 2200 ppb copper. Values are reported as LT50 (hours) with 95% confidence interval. Values sharing a bar are not significantly different. Data are reported for larval of different ages (days post-hatch). MAN values shown with a star are significantly higher from the control values.

<u>MAN</u>				<u>LOK</u>			
29d	unfed	6.7	(4.7-9.4)	29d	unfed	11	(estimated)
25d	unfed	*15.9	(14.2-17.8)	25d	unfed	12.2	(10.8-13.7)
21d	unfed	19.1	(16.8-21.7)	33d	fed	12.3	(9.4-16.1)
21d	fed	21.7	(20.1-23.5)	25d	fed	15.3	(13.9-16.8)
29d	fed	24.9	(21.9-27.1)	21d	unfed	18.4	(16.6-20.3)
25d	fed	*27.5	(24.3-31.1)	9d	unfed	19.4	(17.6-21.4)
9d	unfed	*38.4	(36-41)	21d	fed	23.3	(20.1-27.1)
17d	fed	38.4	(34.7-42.5)	29d	fed	23.4	(20.8-26.1)
9d	fed	*44.8	(42.0-48.0)	17d	unfed	26.3	(24.4-28.3)
17d	unfed	*46.7	(43.3-50.3)	13d	fed	29.2	(25.8-33.0)
13d	fed	*75.0	(69.0-81.6)	9d	fed	31.0	(28.6-33.7)
13d	unfed	*85.3	(82.4-88.2)	17d	fed	33.9	(31.6-36.3)
				13d	unfed	47.0	(36.7-45.0)

Table 5. Further summary of data from Table 4.

<u>MAN</u>		<u>COMBINED</u>	
<u>UNFED</u>	<u>FED</u>	<u>UNFED</u>	<u>FED</u>
29d	21d	MAN 29d	LOK 33d
25d	29d	LOK 29d	LOK 25d
21d	25d	LOK 25d	MAN 21d
9d	17d	MAN 25d	LOK 21d
17d	9d	LOK 21d	LOK 29d
13d	13d	MAN 21d	MAN 29d
		LOK 9d	MAN 25d
		LOK 17d	LOK 13d
		MAN 9d	LOK 9d
		MAN 17d	LOK 17d
		LOK 13d	MAN 17d
		MAN 13d	MAN 9d
			MAN 13d

THE FATE OF TOXIC ORGANIC CHEMICALS IN SEWAGE TREATMENT PLANTS

Brian Clark, Glynn Henry, Donald Mackay, Sandra Salenieks
Institute for Environmental Studies, University of Toronto

ABSTRACT

A predictive model based on the fugacity modelling system, which describes the steady-state fate of organic chemicals in a water pollution control plant has been developed. By estimating a prevailing fugacity in each of the primary, aeration, and secondary settling tanks, chemical concentrations in the water streams, air streams, and sludge streams can be calculated, fluxes can be estimated and a mass balance assembled.

Comparison of the fugacity model with the predictive fate models or sub-models developed by other workers shows good agreement. The fugacity model was also subjected to tests of validity by: (i) conducting laboratory-scale experiments for chemical stripping, stripping-sorption, and stripping-sorption-biodegradation processes; and (ii) comparing the model predictions with data obtained from the literature, from pilot plant studies, and from full-scale water pollution control plants.

The model predicted the fate of organic chemicals with fair accuracy based on reasonable estimates of biodegradation rate constants. It is suggested that when adequately calibrated, the model can be used to give a relatively simple description of the fate of organic chemicals in treatment systems.

INTRODUCTION

Some sixty thousand organic chemicals have been produced commercially and approximately 1200 new chemicals are introduced each year. Many of these chemicals are present in industrial or municipal wastewaters, which are usually treated in a biological oxidation system. The efficiency of these systems is usually expressed as the percent removal of the chemical from the influent stream. This does not necessarily provide information on the amounts of chemical which are biodegraded, stripped or volatilized into the atmosphere, or sorbed onto the biological solids (sludge). A model that predicts the fate of chemicals in a water pollution control plant (WPCP) by determining the amounts and concentrations of the chemical in the effluent, off-gas and waste sludge streams is useful for predicting the true efficiency

of the system, as measured by the actual extent of degradation of the chemical in question. It permits assessment of the impact of each waste stream on the environment as a whole by producing a quantitative picture of the chemical's fate.

A predictive fate model has been developed based on the fugacity modelling concept as proposed by Mackay (1). The model was designed to be easy to understand and use. It is programmed in BASIC language, and is compatible with an IBM Personal Computer. The input parameters are the physical properties of the chemical (molecular weight, vapor pressure, solubility in water, octanol-water partition coefficient, and a degradation rate constant), and the relevant operating parameters of the WPCP (process flowrates, volatile suspended solids concentrations, tank surface areas and volumes). The program gives as output a prediction of the chemical fluxes in all process streams, the chemical concentration in the water, air, and sludge phases and a total statement of mass balance.

A second aspect of the study involved the simulation of a biological treatment plant using a laboratory-scale activated sludge plant to determine the applicability or validity of the model, as well as to determine kinetic rate constants, partition coefficients, and mass transfer coefficients for the processes of bio-oxidation, sorption and stripping. The model was also compared to other predictive fate models, and to data from an actual WPCP.

FUGACITY MODEL

The fugacity model describes and predicts the fate of organic chemicals entering a water pollution control plant based on the following assumptions:

- 1) Equilibrium exists between the water phase and the sludge phase for each tank. In the aeration tank, the off-gas stream is in equilibrium with the water phase.
- 2) The WPCP is at steady state.
- 3) The chemical entering the plant is either dissolved in the water or sorbed on to the incoming suspended solids.
- 4) In both the primary and secondary settling tanks, the sludge blanket volume is ten percent of the total settling tank volume. This estimate is required in order to determine the extent of biodegradation in the settling tanks.

Based on these assumptions, two predictive fate models were developed (to account for either separate waste streams or

combined waste streams). By inputting the following parameters, both programs determine the fugacity in each of the process vessels and hence the concentrations and flow rates:

Chemical Properties - molecular weight (g/mol)
- water solubility (g/m³)
- vapour pressure (Pa)
- log K_{ow} (ie. octanol-water partition coefficient)
- first order biodegradation rate constants in the aeration tank and the primary and secondary settling tanks (h⁻¹)

System Properties - volumetric flow rates (m³/h) and volatile suspended solids concentrations (g/m³) for:
i) influent stream
ii) raw sludge stream
iii) primary effluent stream
iv) mixed liquor stream
v) return sludge stream
vi) waste sludge stream
vii) secondary effluent stream
viii) air stream

- tank volumes (m³)
- primary and secondary settling tank surface areas (m²)
- MLSS concentration (g/m³)
- temperature (K)

A full account of the model structure and mathematics is beyond the scope of this report, but reference can be made to Clark (1986) for more detail. A brief review is presented below.

Fugacity and its use in modelling systems has been described in a series of papers by Mackay et al (1). It can be viewed as an escaping tendency of partial pressure. When a chemical such as benzene is in equilibrium between phases such as water, air and biomass, its fugacity is equal in all three phases. Fugacity (f) is related to concentration (C) by the simple expression:

$$C = Zf$$

where Z is a fugacity capacity for the chemical in the particular phase. Procedures have been published by which Z values can be estimated for all relevant phases, mainly from partition coefficients and properties such as water solubility and vapour pressure.

All process rates are expressed as the products of the fugacity in the relevant phase and a D value, ie.,

$$\text{Rate} = Df$$

Procedures for estimating D values have been documented, but a brief review may be useful here.

Reaction or degradation rates can be characterized by a reaction D value defined as VZk , where V is the phase volume, Z is the fugacity capacity and k is the first order rate constant. The group Df is thus equivalent to VCK . This expression is used to describe biodegradation rates. Non-linear kinetics can be included but first-order behaviour is generally assumed to apply to dilute chemical components.

Transfer by flow from vessel to vessel is characterized by a D value defined as GZ , where G is the phase flow rate and Z is the fugacity capacity. The rate Df is thus GC . When the flow is of a mixture (eg. water and biomass), separate D values are defined, then added, and the amounts transported in each phase can be calculated. This expression is used for water, biomass and air flows.

The rate of diffusive transfer between phases such as water and air by evaporation or stripping can be expressed as $D(f_1-f_2)$, where f_1 is the chemical fugacity in the source and f_2 in the destination phase. This is used to describe evaporation, D being defined as:

$$1/D = 1/k_1AZ_1 + 1/k_2AZ_2$$

where k_1 is the water side and k_2 is the air side mass transfer coefficients (units of velocity), A is the interfacial area, and Z_1 and Z_2 are the water and air Z values. This is essentially the Whitman two resistance model as used by previous workers.

For air stripping a similar approach could be used, but the individual values of k_1 , k_2 and A are uncertain and it is useful to define a product of mass transfer coefficient and area. In the interests of simplicity, we assume that the D value is so large that f for air equals that of water, ie. the streams are in equilibrium. Non-equilibrium could be treated by including a suitable D value describing the transfer resistance.

A simple mass balance can be assembled as depicted in Figs. 1 and 2. The various input parameters are used to calculate the D and Z values and the equations solved as shown to give the fugacities. The concentrations can then be calculated as fZ and the flows as Df.

There is no need for the user to understand or use fugacity since this is handled within the program. It is possible to rewrite the equations in Fig. 2 in conventional concentration form, but the final conventional equations are very lengthy. The conventional and fugacity equations are ultimately algebraically identical. The fugacity format equations are more compact and elegant, and with some effort, give more easily understandable results.

Fig. 1: Fate of Organic Chemicals in a Simple Activated Sludge Plant

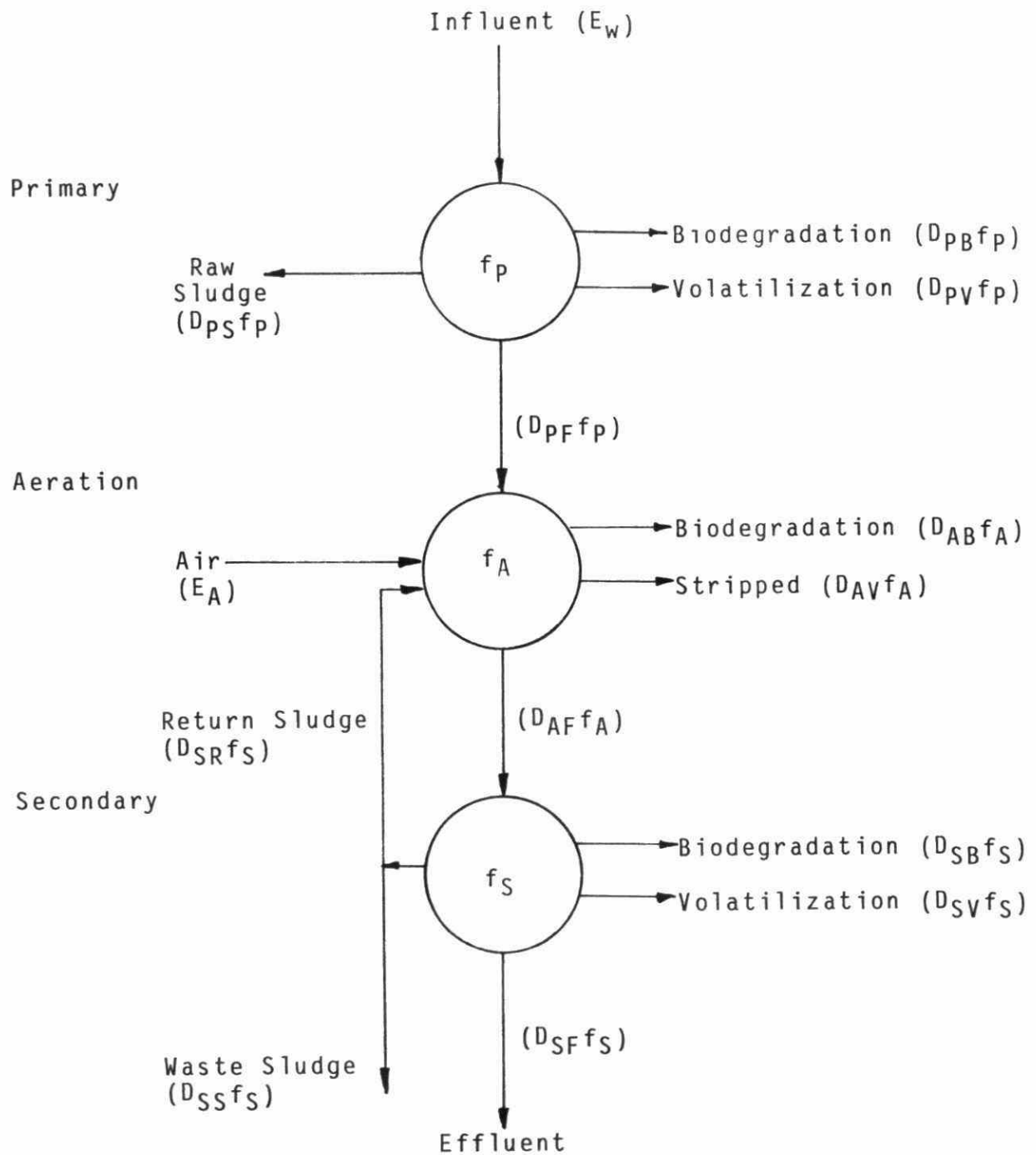


Fig. 2: Mass Balance Equations

Primary Tank

$$E_W = (D_{PS} + D_{PF} + D_{PB} + D_{PV})f_P = D_{PT}f_P$$

Aeration Tank

$$E_A + D_{PF}f_P + D_{SR}f_S = (D_{AB} + D_{AV} + D_{AF})f_A = D_{AT}f_A$$

Secondary Tank

$$D_{AF}f_A = (D_{SB} + D_{SV} + D_{SF} + D_{SR} + D_{SS})f_S = D_{ST}f_S$$

Solution:

$$f_P = E_W/D_{PT}$$

$$f_A = (E_A + D_{PF}f_P)/(D_{AT} - D_{AF}D_{SR}/D_{ST})$$

$$f_S = D_{AF}f_A/D_{ST}$$

where D_{PT} , D_{AT} and D_{ST} are as defined above.

Sorption to biomass was treated using an approach similar to Blackburn's (1984), which regards the biomass as consisting of 20% (volume fraction) octanol, and 80% water, i.e.,

$$Z_b = 0.2K_{ow}Z_w + 0.8Z_w$$

Biodegradation is treated as a first-order decay process. Rate constants can be defined based on the total chemical concentration or the concentration actually present sorbed onto the biomass. Since most experiments report decay in total concentrations, the former is preferred. The major challenge in modelling WPCPs is to select an appropriate value for this rate constant. The most convenient methods are to select an appropriate half life based on results of bench scale tests, or to fit the model to some actual performance data from pilot or full scale plants. An advantage of the model is that it "subtracts out" the losses attributable to sorption to sludge,

The output from this program can be printed in any combination of the following three forms as shown in Fig. 3:

- 3A) data sheet
- 3B) schematic diagram of the WPCP
- 3C) narrative summary.

Fig. 3A: Data Summary Sheet

XYZ

Chemical Properties:

Molecular Weight (g/mol)	100
Aqueous Solubility (g/m ³)	10
Vapour Pressure (Pa)	9.869232E-05
(atm)	7.500616E-02
(mm Hg)	10
Octanol-Water Partition Coeff (K _{ow})	1
LOG K _{ow}	1
Biodegradation Rate Constant (h ⁻¹)	.01
-Primary Tank	.01
-Aeration Tank	.01
-Settling Tank	.01

System Properties:

Primary Tank:

Water Influent Rate [m ³ /h]	1000
Chemical Concentration In Plant Influent [g/m ³]	.01
Primary Sludge Removal Rate [m ³ /h]	100
Primary Sludge VSS Concentration [g/m ³]	1000
Primary Effluent VSS Concentration [g/m ³]	10
Influent VSS [g/m ³]	150
Primary Tank Volume [m ³]	1000
Primary Tank Surface Area [m ²]	100
Hydraulic Retention Time (h)	1

Aeration Tank:

Air Flowrate [m ³ /h]	1000
Sludge Recycle Rate [m ³ /h]	100
Aeration Tank Volume [m ³]	1000
MLSS Concentration [g/m ³]	2000
Hydraulic Retention Time (h)	1.11
Solids Retention Time (h)	18.5
(days)	.771
Temperature [°C]	25

Settling Tank:

Waste Sludge Removal Rate [m ³ /h]	100
Underflow VSS Concentration [g/m ³]	1000
Effluent VSS Concentration [g/m ³]	10
Settling Tank Volume [m ³]	1000
Settling Tank Surface Area [m ²]	100
Hydraulic Retention Time (h)	.99

Tank	Phase	Fugacity (Pa)	Concentration (g/m ³)	(mol/m ³)
Primary	Water	9.958018E-03	9.958018E-03	9.958018E-05
	Sludge	9.958018E-03	1.991604E-02	1.991604E-04
Aeration	Air	9.509096E-03	3.83614E-04	3.83614E-06
	Water	9.509096E-03	9.509096E-03	9.509096E-05
	Sludge	9.509096E-03	1.901819E-02	1.901819E-04
Settling	Water	9.488111E-03	9.488109E-03	9.488111E-05
	Sludge	9.488111E-03	1.897622E-02	1.897622E-04

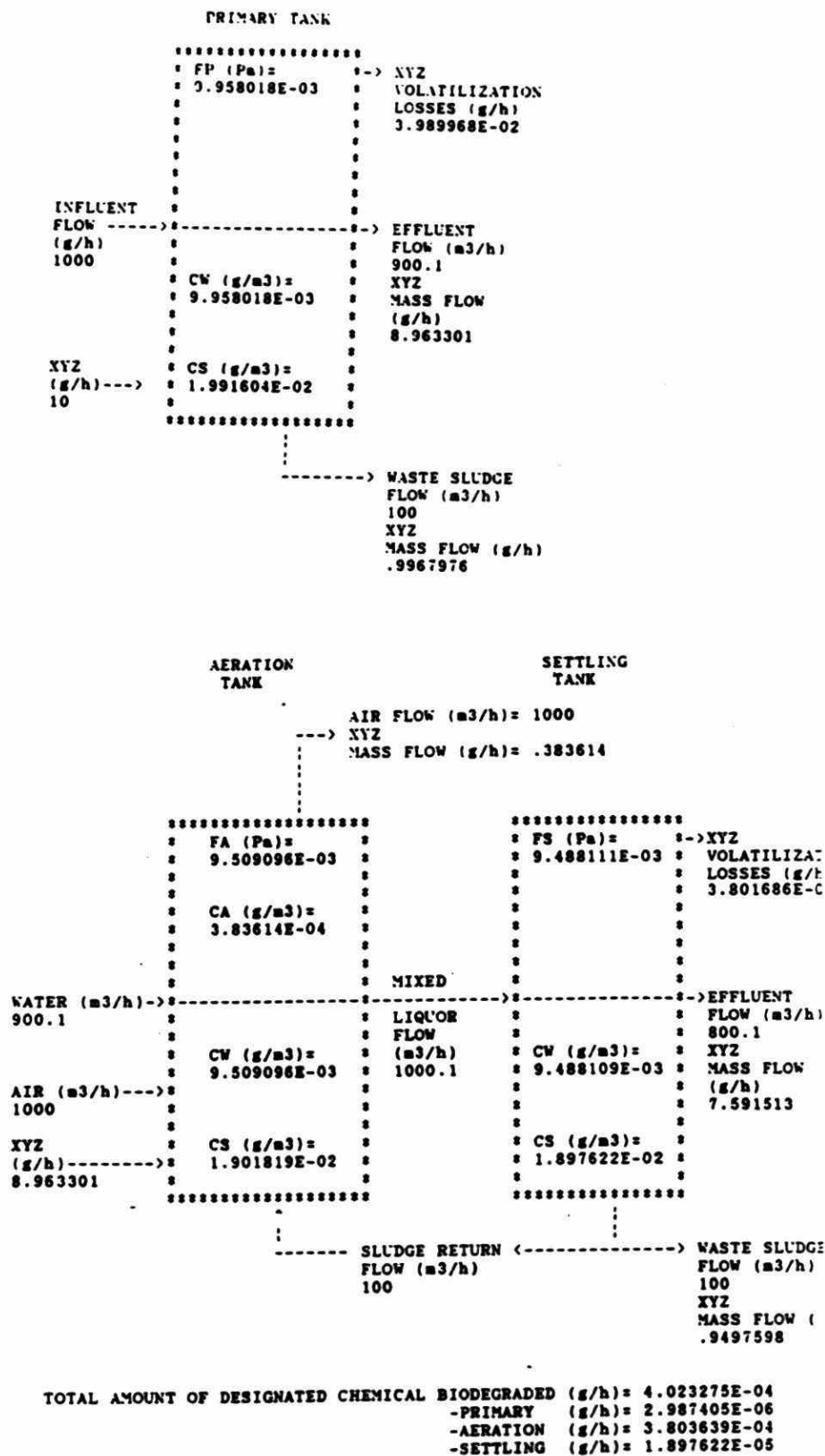
WPCP Mass Balance for XYZ

WPCP Stream Directory:



Stream # No.	Stream Flow m ³ /h	Chemical Flow Grams/h	Mols/h	Percent
Primary Tank				
1. Influent	1000	10	.1	100
2. Effluent	900.1	8.963301	.089633	
3. Waste Sludge	100	.9967876	9.967976E-03	9.967976
Volatilized		3.989968E-02	3.989968E-04	.3989968
Biodegraded		2.987405E-06	2.987405E-08	2.987405E-05
Aeration Tank				
4. Air Inlet	1000	0	0	
5. Air Outlet	1000	.383614	3.83614E-03	3.836139
6. Mixed Liquor	1000.1	9.529067	9.529067E-02	
Biodegraded		3.803639E-04	3.803638E-06	3.803638E-03
Settling Tank				
7. Effluent	800.1	7.591513	7.591513E-02	75.91513
8. Return Sludge	100	.9497598	9.497598E-03	
9. Waste Sludge	100	.9497598	9.497598E-03	9.497598
Volatilized		3.801686E-02	3.801686E-04	.3801686
Biodegraded		1.897622E-05	1.897622E-07	1.897622E-04

Fig. 3B: Schematic Diagram of WPCP



Legend:

FP: Fugacity in the primary tank
FA: Fugacity in the aeration tank
FS: Fugacity in the settling tank
CA: Concentration of chemical in air
CW: Concentration of chemical in water
CS: Concentration of chemical in sludge

Inflow

The chemical of concern enters the plant at a concentration of 0.010 g/m in a total water flow of 1000.0 m³/h. Therefore, 10.000 g/h of the chemical enters the plant.

Primary Settling Tank

During primary treatment, the chemical of concern is 0.02 percent removed due to being sorbed into the volatile suspended solids present in the primary tank. It is estimated that 0.40 percent is volatilized into the atmosphere. Biodegradation accounts for a 0.00 percent reduction of the chemical. This behavior determines the primary effluent concentration to be 0.0100 g/m³ in the water and 0.01992 g/m³ in the sludge.

Aeration Tank

The primary effluent enters the aeration basin at a flowrate of 900.1 m³/h. The air flowrate into the tank is 1000.0 m³/h. Under these conditions, the chemical is estimated to be 3.84 percent removed due to stripping and 0.00 percent removed due to biodegradation. This results in a sludge concentration of 0.01902 g/m³ and a water concentration of 0.0095 g/m³. The concentration of the chemical in the off-gas stream is 0.0004 g/m³.

Secondary Settling Tank

After aeration, the mixed liquor, flowing at 1000.1 m³/h into the secondary tank, is allowed to settle. This results in the volatilization of 0.38 percent of the chemical of concern as well as a decrease of 0.00 percent due to biodegradation. It is therefore estimated that the effluent water concentration is 0.0095 g/m³ in a stream flowing at 800.1 m³/h. The underflow is divided into two streams; return sludge and waste sludge which flow at 100.0 m³/h and 100.0 m³/h respectively. The chemical concentration in the sludge is 0.0190 g/m³.

Overall Summary

Assuming that the chemical enters the plant at a flow of 10.0 g/h, 0.78 percent or 0.1 g/h of the chemical will volatilize into the atmosphere, 3.84 percent or 0.4 g/h is stripped, and 0.00 percent or 0.0 g/h is biodegraded.

Also, the primary sludge stream removes 9.97 percent or 1.0 g/h, and the secondary waste sludge stream removes 9.50 percent or 0.9 g/h.

The concentration of the chemical in the air off-gas is 0.0004 g/m³. The primary sludge concentration is 0.02 g/m³; and the secondary sludge concentration is 0.02 g/m³.

The secondary effluent concentration is 0.0095 g/m³. This determines that the water pollution control plant is 24.08 percent effective for the removal of XYZ.

The data sheet lists the input data, followed by a table which details the water, sludge and air concentrations, as well as the fugacity for each of the primary, aeration, and secondary tanks. The data sheet is also supplemented with a chart showing the chemical mass fluxes in each process stream.

The schematic diagram uses a "black-box" approach to symbolize each tank. The picture provides data on the volumetric flowrates of each process stream, the mass flux of the chemical in each stream, as well as the fugacity, water, air and sludge concentrations in each vessel.

The narrative summary is a one page summary of the plant flows and chemical concentrations in each phase in each tank. The summary also provides an overall statement of the fate of the chemical in the WPCP.

EXPERIMENTAL

A series of experiments were performed to obtain verification data for the model using a bench-scale completely mixed activated sludge plant. A flow diagram of the apparatus is shown in Figure 4. Where possible, glass was used to minimize adsorption of the chemicals to the walls of the vessels.

To validate the model for general use, and to cover a wide range of chemical properties (water solubility, vapor pressure, octanol-water partition coefficient and biodegradation rates), the four chemicals toluene, chlorobenzene, naphthalene and pentachlorophenol were studied.

A concentrated solution of the chemicals was prepared by dissolving each chemical in a pure methanol solution which was then injected into the aeration tank. This method of entry ensured that the chemicals were in dissolved or sorbed form, and not present as a separate phase.

Stripping studies were conducted in a pure water system without biomass in order to determine the fate of the chemical at various air (0.33 to 3 L/min), water (12.5 to 25 mL/min), return sludge (4 to 7.5 mL/min), and chemical (0.07 to 0.9 g/min) flowrates. These results were then compared to the predictions by the model.

Dead biomass, consisting of sludge autoclaved three times at 121°C and 202.7 kPa for 15 minutes, was introduced into the stripping apparatus to determine the effect of sorption on the fate of the chemicals. Air, water, and sludge samples were analyzed to determine the concentration of the chemical in each phase. These results were then compared to the model predictions.

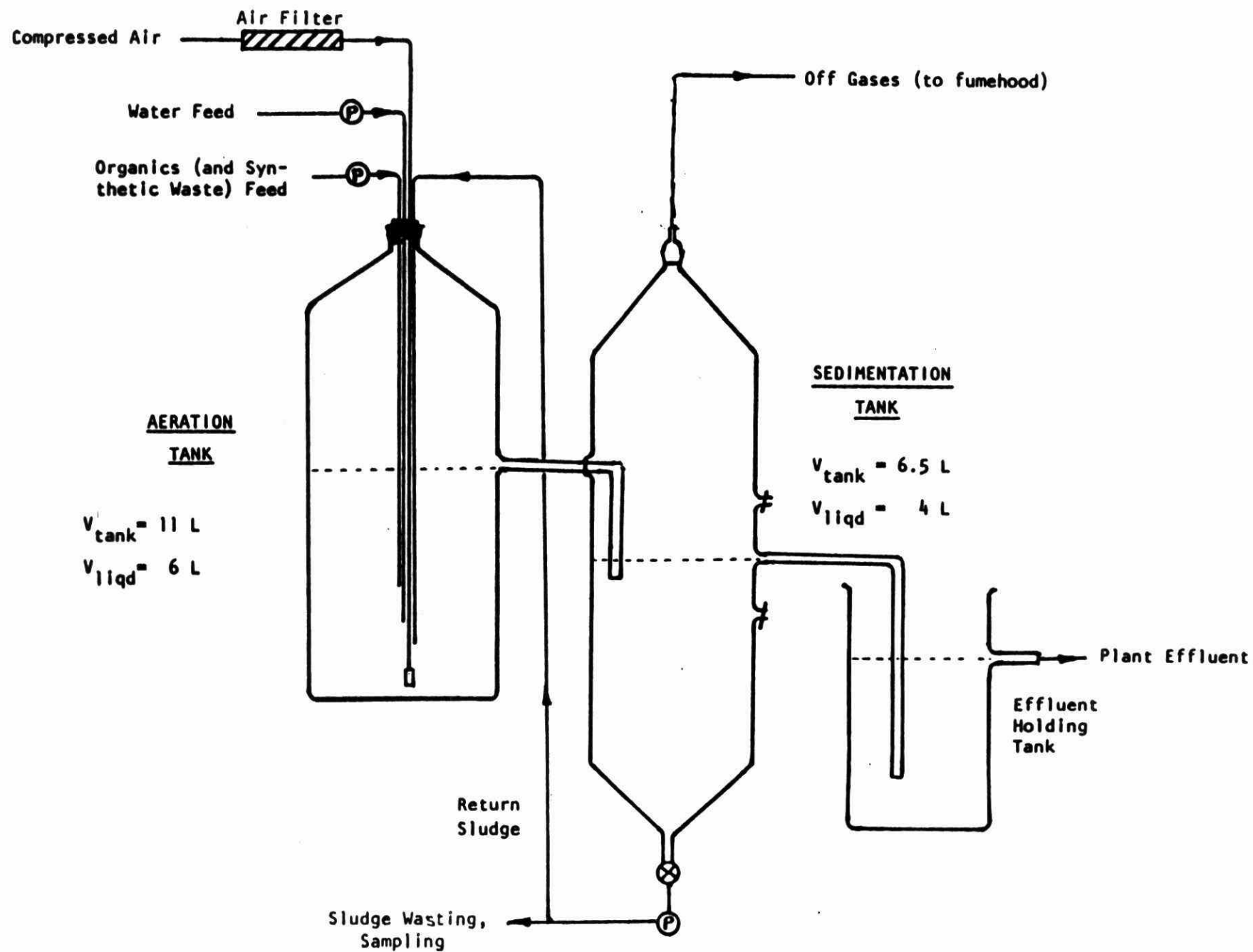


Fig. 4: Laboratory Activated Sludge Plant

The third stage of the experiment consisted of adding active biomass into the system to study its effects on the fate of the chemicals of concern. The activated sludge used for the seeding of the reactors was obtained from a local municipal activated sludge plant. The bench-scale units were initially fed a synthetic waste comprised of peptone, beef extract and inorganic nutrients until stable operation of the activated sludge reactors was achieved. The chemicals were then added to the influent at low concentrations to allow the activated sludge to become acclimated to the chemicals. The systems were operated at a hydraulic retention time of 7 to 8 hours, with a mean cell residence time of approximately 7 days.

Water samples were analyzed by solvent extraction using hexane. The samples were analyzed on a gas chromatograph equipped with a flame ionization detector, and a stainless steel column packed with 10% SE-30 P, AW-DMCS, 60/80. The accuracy of extraction was evaluated by computing the recovery in spiked samples.

Air samples were collected by diverting a known fraction of the off-gas stream through a liquid nitrogen cooled collection trap. After approximately 1 hour sampling, the trap was removed from the Dewar flask, the contents were extracted using hexane, and the extract was analyzed by GC.

For the sorption and biodegradation experiments, the concentration of the chemical sorbed on the sludge was determined by centrifuging sludge samples, followed by Soxhlet extraction for 4 hours using hexane as the solvent. The hexane was collected and analyzed by GC.

RESULTS AND DISCUSSION

The general aim of the series of experiments was to establish a mass balance for the chemical under various treatment regimes, ranging from simple air stripping tests to a full simulation of stripping, biosorption and biodegradation. The amounts biodegraded could only be inferred by difference. It is believed that the most relevant expression of the results is as percentages by mass of the amount of chemical fed to the system, as accounted for in the various exit streams. These amounts were estimated from flowrates and concentrations. The general aim of the project is to establish a capability of predicting these percentages in full scale plants. Only a brief review of results is presented here.

The experimental and predicted mass balance concentrations for the stripping tests agreed well, with up to 16% difference. In most cases, the overall mass balance recovery was over 96%.

In the stripping-sorption tests, the water, air, and sludge

concentrations were in fair agreement with the predicted results, but there was considerable difficulty in achieving satisfactory mass balances.

The validation of the model for combined stripping-sorption-biodegradation proved to be very difficult as a result of the operational problems with the laboratory-scale activated sludge plant. However, a total of nine experiments were conducted and biodegradation rate constants estimated.

In general, it was found that with the resources and facilities available, it was exceptionally difficult to maintain a steady-state laboratory scale activated sludge plant. There were frequent interruptions due to component failure, usually at night when the systems were unsupervised. Similiar experiences have been reported by other groups and we have concluded that to obtain reliable data, it is necessary to have at least a facility and services comparable to those of the Environment Canada facility at Burlington.

Other Validation Approaches

Three other approaches to model validation or calibration are being pursued.

First, the model is being applied to data obtained from other groups, mainly in the US, for example in Oklahoma, Purdue, Cincinnati, and Michigan.

Second, the model is being compared in predictive performance to other models. This is not a validation, but it should highlight any major discrepancies.

Finally, an attempt is being made to apply the model to actual operating data from WPCPs, for example at Hamilton. Ultimately, this is the most useful data and represents an essential calibration. Because of the variable nature of WPCPs, it is likely that laboratory simulators will never satisfactorily mimic full scale performance. If the model can be used to correlate and even predict full scale performance, it will be an invaluable tool for the rational assessment of the fate of toxic organic chemicals in WPCPs, and could thus play a useful role in regulating discharges to municipal collection systems to levels judged to be sufficiently low that, after treatment, the receiving water, air and sludge are not adversely affected by the various effluents from the plants. This is the goal of the present research effort.

CONCLUSIONS

A fugacity modelling system has been developed which can predict the phase concentrations and process stream fluxes in a wastewater treatment plant based on the properties of the chemical (molecular weight, water solubility, vapour pressure, octanol-water partition coefficient, and biodegradation rate constant) and the operating parameters of the treatment plant. The model is compatible with an IBM Personal Computer and is simple to use.

The model output correlates well with models proposed by other workers such as Blackburn (3), Roberts (4), and Kincannon and Weber (3). It predicts with reasonable accuracy the fate of organic chemicals as determined in a laboratory-scale pollution control plant. It is currently being tested using data from other laboratory and full scale systems. It is believed that the model structure is based on sound physical, chemical and biological principles, and should, when validated, be capable of adequately simulating the performance of full-scale treatment plants.

REFERENCES

1. Mackay, D., Paterson, S., "Calculating Fugacity", Environ. Sci Technol., 15(9), 1006-1014 (1981).
2. Clark, B.E., "A Predictive Fate Model for Organic Chemicals in a Water Pollution Control Plant", MASC Thesis, Dept. of Chemical Engineering, University of Toronto, (1986).
Interface", Nature, 247, 181-184 (1974).
3. Blackburn, J.W., Troxler, W.L., Sayler, G.S., Breen, A., Yagi, O., "Prediction of the Fates of Organic Chemicals in Activated Sludge Wastewater Treatment Processes", Draft Publication, Contracts 68-03-3027, Work Assignments 1 and 6, 68-03-3074, Work Assignment 2, November, 1983.
4. Roberts, P.V., Dandliker, P.G., "Mass Transfer of Volatile Organic Contaminants from Aqueous Solution to the Atmosphere during Surface Aeration", Environ. Sci. Technol., 17, 484-489 (1983).

Fig. 5: Definition of "D" Values

E_W = emissions into primary tank (mol/h)

$D_{PS} = G_{PWS}Z_W + G_{PBS}Z_B$ (ie. chemical flow in raw sludge)

where G_{PWS} is water flow in raw sludge stream (m^3/h)

G_{PBS} is biomass flow in raw sludge stream (m^3/h)

Z_W is water fugacity capacity (mol/ $m^3 \cdot Pa$)

Z_B is biomass fugacity capacity (mol/ $m^3 \cdot Pa$)

$D_{PB} = V_{PB}k_{PB}Z_B$ or $V_{PT}k_{PT}Z_{TP}$ (ie. biodegradation in primary tank)

where V_{PB} is biomass volume in primary tank (m^3)

V_{PT} is total volume in primary tank (m^3)

V_{PW} is water volume in primary tank (m^3)

k_{PB} is rate constant for biodegradation based on concentrations in biomass (h^{-1})

k_p is rate constant for biodegradation based on total concentration in water and biomass (h^{-1})

Z_{TP} is overall fugacity capacity in primary tank defined as $(V_{PW}Z_W + V_{PB}Z_B)/V_{PT}$

k_{PT} and k_{PB} are related by $k_{PB} = k_p(1 + V_{PW}/(V_{PB}K_{BW}))$
 $= \frac{k_p(\text{total chemical present})}{\text{amount of chemical in biomass}}$

$1/D_{PV} = (1/k_{WP}A_pZ_W) + (1/k_{AP}A_pZ_A)$ (ie. volatilization from primary tank)

where k_{WP} is water side mass transfer coefficient in primary tank (mol/h)

k_{AP} is air side mass transfer coefficient in primary tank (mol/H)

A_p is surface area of primary tank (m^2)

Fig. 5 cont.

$$D_{PF} = G_{PWF}Z_W + G_{PBF}Z_B \quad (\text{ie. chemical flow from primary tank to secondary tank})$$

where G_{PWF} is water flow from primary to aeration tank (m^3/h)

G_{PBF} is biomass flow from primary to aeration (m^3/h)

E_A = input of chemical in input air (usually zero) (mol/h)

$D_{AB} = V_{AB}k_{AB}Z_B$ or $V_{AT}k_{AT}Z_{AT}$ (ie. biodegradation in aeration tank)
variables defined similarly as for primary tank, but for aeration tank

$$D_{AV} = G_A Z_A \quad (\text{ie. stripping from aeration tank})$$

where G_A is aeration rate, or more specifically the flow rate of air which becomes saturated with chemical (m^3/h)

$$D_{AF} = G_{AWF}Z_W + G_{ABF}Z_B \quad (\text{ie. chemical flow from aeration to secondary tank})$$

where G_{AWF} is water flow from aeration to secondary (m^3/h)

G_{ABF} is biomass flow from aeration to secondary (m^3/h)

$$D_{SB} = V_{SB}k_{SB}Z_B \text{ or } V_{ST}k_{ST}Z_{ST}$$

variables defined similarly as for primary tank, but for secondary tank

$$1/D_{SV} = 1/(k_{WS}A_S Z_W) + 1/(k_{AS}A_S Z_A) \quad (\text{ie. volatilization from secondary tank})$$

variables defined as for volatilization from primary tank

$$D_{SF} = G_{SWF}Z_W + G_{SBF}Z_B \quad (\text{ie. chemical in final effluent})$$

where G_{SWF} is water flow rate in final effluent (m^3/h)

G_{SBF} is biomass flow rate in final effluent (m^3/h)

TOXICITY OF PENTACHLOROPHENOL TO ZOOPLANKTON

by

N.K. Kaushik and G. Stephenson
Department of Environmental Biology
University of Guelph
Guelph, Ontario N1G 2W1

INTRODUCTION

Approximately 3.4 million kilograms of chlorinated phenols (CP) are used annually in Canada; 80% of these are used in the form of pentachlorophenol (PCP), which is used as a wood preservative and in other activities associated with the forestry industry (Hoos, 1978).

In the U.S.A., 85% of human urine samples tested had mean concentrations of 6 ppb of PCP (cf. Cirelli, 1978). No similar study has been conducted in Canada; however, PCPs have been identified in samples of water, sediment, snow melt, agriculture produce, sewage effluent, landfill leachates and even aquatic biota (snails, fish, crayfish). Wood-preserving plants are located across the country with the highest concentration of both pressure and non-pressure treatment plants located in Ontario. An extensive survey of the Great Lakes Basin for detectable levels of PCP and of 85 whole bulk water samples collected, only 8 sites produced samples with no detectable PCP (Jones, 1981). Lake Ontario and the Bay of Quinte contained the highest concentrations (< 5 ng/L to 23,000 ng/L) (Fox and Joshi, 1984). Other designated routes of entry into the aquatic environment were on-site application of preservatives to wood products, petrochemical drilling fluids, aqueous chlorination, pulp and paper mill wastewaters, tanneries and industrial cooling systems. Despite this, almost ubiquitous distribution of PCP in the environment, there remains a paucity of scientific data regarding the fate and effects of PCP (Inglis and Davis, 1972; Adelman and Smith Jr.,

1976; Mattson et al. 1976; Guo et al., 1979) in aquatic ecosystems, which are, in many cases, the final sinks for such toxicants.

Toxicity of PCP to fish has been investigated and the effects of PCP on laboratory cultures of algae has been studied to a limited extent (Gelfaud, 1941; Palmer and Maloney, 1955; Enigk and Duwel, 1960), but comprehensive studies on the effects of PCP on freshwater zooplankton especially under Canadian conditions are limited (Jones, 1981). Secondary producers, in particular the cladoceran zooplankton, that feed primarily on phytoplankton and/or detritus are essential to transfer of energy within aquatic systems. Zooplankton are the major dietary component of planktivorous fish and the sole dietary requirement of some immature stages of fish. They are also essential to the cycling of nutrients in lakes.

Chlorinated phenols (CPs) including PCP are in Category II of Environment Canada's list of Priority Chemicals and as such are regulated by Agriculture Canada under the Pest Control Products Act. Concern regarding fate and effects of CPs and their formulated impurities in the environment has been expressed in a technical review (Jones, 1981) and changes in the regulatory status of the chlorophenols appear imminent.

With this background in mind, we initiated studies to determine toxicity of pentachlorophenol with three age classes of Daphnia magna and with adult Daphnia galeata mendotae. Our main objectives were to determine acute and chronic toxicity of pure and technical formulations of PCP to the above two species of zooplankton, to determine effects of pH and temperature on toxicity of these formulations and to determine bioaccumulation and bioconcentrations of PCP in zooplankton. The present paper describes only preliminary results dealing with some of the objectives and the investigation is still in progress.

MATERIALS AND METHODS

Acute Toxicity of Two Formulations of Pentachlorophenol

A pure formulation (99%) of pentachlorophenol was obtained from Aldrich Chemicals, Milwaukee, Wisconsin, and a technical formulation (86%) from Stanchem, Toronto, Ontario. A series of acute static toxicity tests were performed for both these formulations with three age classes (young, juvenile, and adult) of D. magna and with adult D.g. mendotae.

Test solutions were made from the stock solutions by dilution with aerated well water (pH 7.5-7.8, alkalinity 223 ± 4.8 mg/L, particulate organic carbon 1.1 ± 0.4 , dissolved organic carbon 0.5 ± 0.1 mg/L). A test consisted of nine treatments - eight concentrations of PCP (0.75, 1.0, 1.5, 2.0, 2.5, 3, 4, and 5 mg/L) that encompassed a response range of 0 to 100% mortality, and controls with an acetone equivalent of the maximum PCP concentration. Each treatment had five replicate beakers with 80 mL of a given test solution and five daphnids were placed in each beaker for a total of 25 daphnids per treatment. The exposure durations of 24, 48, and 72 h occurred under controlled conditions with a photoperiod of 16 light h: 8 dark h and a constant temperature of $20 \pm 1^{\circ}\text{C}$. The results of the acute toxicity tests were summarized by comparing the estimated LC_{50} values using analyses of variance followed by DMRT procedures (PARAMETRIC, ANOVA, DUNCAN; TERRY JAMES, UNIVERSITY OF GUELPH). Values were derived from probit analyses (PARAMETRIC, PROBIT; TERRY JAMES, UNIVERSITY OF GUELPH) using an IBM-PC.

Chronic Toxicity Tests of Two Formulations of Pentachlorophenol

A chronic toxicity study consisting of eight treatments was conducted with D. magna. The treatments included acetone controls, four nominal sublethal concentrations of technical PCP (0.01, 0.05, 0.1, and 0.5 mg PCP/L) and three nominal sublethal concentrations of pure PCP (0.01, 0.05 and 0.1 mg

PCP/L). There were 20 daphnids in each treatment, one daphnid per beaker with 80 mL of test solution in each beaker. Experimental conditions were comparable to those in the acute toxicity tests. The test solutions were changed every second day at which time the animals were fed 2.5 mg green algae/L. The daphnids were checked daily and twice to appearance of the primiparous instar, twice to release of first brood, number of young produced, adult mortality, the number of moults and appearance of ephippia recorded. The experiment was terminated when all of the daphnids had expired.

Interaction of Low pH and Acute Toxicity of Pentachlorophenol

Acute toxicity test procedures as described previously were repeated with *D. magna* and *D.g. mendotae*, only the pH of the well water was lowered from 7.8 to 5.5 (± 0.5) by addition of 0.1 N sulfuric acid. The pH of the test solutions in each beaker was measured every 11 h and adjusted when necessary by additions of minute quantities of sulfuric acid in order to maintain a constant pH over a 48 h period. At this time the test organism was removed temporarily from its container and we found no effect on survival of the daphnids by this additional handling. The pH was measured with a Nester pH pen.

RESULTS

Acute Toxicity of PCP

The toxicity of technical and pure PCP to daphnids was influenced by both exposure duration, age of organism and species of test organism. Young *D. magna* were equally susceptible to technical and pure PCP, whereas the juvenile and adults were less tolerant of the pure pentachlorophenol (Table 1). Pure PCP was more toxic to juveniles at 48 and 72 h exposure durations and more toxic to adults at all exposure durations (Table 1). The pure PCP was equally toxic to all age classes of *D. magna* regardless of exposure time, but *D. magna*

young were less tolerant of technical PCP than were juveniles and adults (Table 2). D. magna was much more sensitive to pentachlorophenol regardless of the type of formulation than was D. galeata mendotae (Table 3).

PCP did not affect the time of appearance of the primiparous instar (Table 4) nor the time to release of the first brood (Table 5). The average number of young produced per female exposed to both technical and pure PCP was not significantly different from those in the controls (Table 6). Although the average number of broods produced per female was higher in individuals exposed to PCP, the difference was not significant at $P \leq 0.05$ (Table 7). Also, the brood size of control individuals was not significantly higher than individuals exposed to both technical and pure pentachlorophenol (Table 8). In short, there was no effect of the various sublethal concentrations of technical and pure pentachlorophenol on the reproductive parameter of D. magna.

The sublethal concentrations of both technical and pure pentachlorophenol did not affect the longevity of D. magna as the survivorship curves were not significantly different from those in the controls (Fig. 1) with individuals surviving for an average of 103 days in the controls and 116, 114, 116 and 112 days in the technical formulation 0.01, 0.05, 0.1, 0.5 mg PCP/L, respectively. The mean survival time of daphnids exposed to pure PCP was 116, 109, and 118 days for 0.01, 0.05 and 0.1 mg PCP/L, respectively.

Influence of Low pH on Acute Toxicity of Pure and Technical PCP to Adult Daphnids

The mean 48 h LC_{50} estimates for adult D. magna exposed to technical and pure PCP at a pH of 5.5 were 0.88 and 0.58 mg PCP/L, respectively ($n = 3$). The mean 48 h LC_{50} estimates for D. magna exposed to pentachlorophenol test solutions with a pH of 7.8 were 2.79 and 1.78 mg PCP/L for technical and pure,

Table 1. LC₅₀ estimates (mg/L; mean \pm SD for two formulations of PCP and three age classes of D. magna.

Age Class	PCP Formulation	Exposure Duration (h)		
		24	48	72
Young (24 \pm 12 h)	Technical	1.84 \pm 0.33	1.70 \pm 0.28	1.53 \pm 0.38
	Pure	1.87 \pm 0.38	1.50 \pm 0.19	1.37 \pm 0.19
Juvenile (48-96 h)	Technical	2.98 \pm 0.57	2.39 \pm 0.48	2.21 \pm 0.44
	Pure	2.22 \pm 0.18	1.54 \pm 0.15	1.15 \pm 0.30
Adult	Technical	3.91 \pm 1.15	2.79 \pm 0.56	2.46 \pm 0.39
	Pure	2.63 \pm 0.44	1.78 \pm 0.55	1.27 \pm 0.61

LC₅₀ estimates joined by a vertical line are not significantly different at $P \leq 0.05$.

Table 2. A comparison of the LC₅₀ estimates (mg/L; mean \pm SD) for three age classes of D. magna exposed to technical and pure formulations of PCP.

PCP Formulation	Age Class	Exposure Duration (h)		
		24	48	72
Technical	Young	1.84 \pm 0.33	1.70 \pm 0.28	1.53 \pm 0.38
	Juvenile	2.98 \pm 0.57	2.39 \pm 0.48	2.21 \pm 0.44
	Adult	3.91 \pm 1.15	2.79 \pm 0.56	2.46 \pm 0.39
Pure	Young	1.87 \pm 0.38	1.50 \pm 0.19	1.37 \pm 0.19
	Juvenile	2.22 \pm 0.18	1.54 \pm 0.15	1.15 \pm 0.30
	Adult	2.63 \pm 0.44	1.78 \pm 0.55	1.27 \pm 0.61

LC₅₀ estimates joined by lines are not significantly different at $P \leq 0.05$.

Table 3. Mean LC_{50} estimates for adult D.g. mendotae exposed to two formulations of PCP.

PCP Formulation	Exposure Duration (h)	
	24	48
Technical	0.053	0.059
Pure	0.058	0.057

LC_{50} estimates joined by lines are not significantly different at $P \leq 0.05$.

Table 4. Average time of appearance of the primiparous instar in the brood chamber (days).

Criterion 1	Time (days) $\bar{x} \pm SD$
Control	7.54 ± 1.2
Technical - PCP	6.94 ± 1.3
Pure - PCP	7.12 ± 0.9

Table 5. Average time to release of the first brood in each treatment (days).

Criterion 2	Time (days) $\bar{x} \pm SD$
Control	12.86 ± 0.84
Technical - PCP	13.10 ± 1.21
Pure - PCP	12.91 ± 0.92

Table 6. Average number of young produced per female per treatment.

		Concentration				
		0	0.01	0.05	0.1	0.5
Control	\bar{x}	285	-	-	-	-
	SD	102				
Technical PCP	\bar{x}	-	291	303	326	239
	SD		79	96	76	60
Pure PCP	\bar{x}	-	279	259	276	-
	SD		71	75	66	

Table 7. Average number of broods per female per treatment.

		Concentration				
		0	0.01	0.05	0.1	0.5
Control	\bar{x}	24.84	-	-	-	-
	SD	8.27				
Technical PCP	\bar{x}	-	27.55	27.30	29.32	26.10
	SD		7.20	8.72	7.20	6.68
Pure PCP	\bar{x}	-	27.75	25.25	27.05	-
	SD		6.56	7.78	6.84	

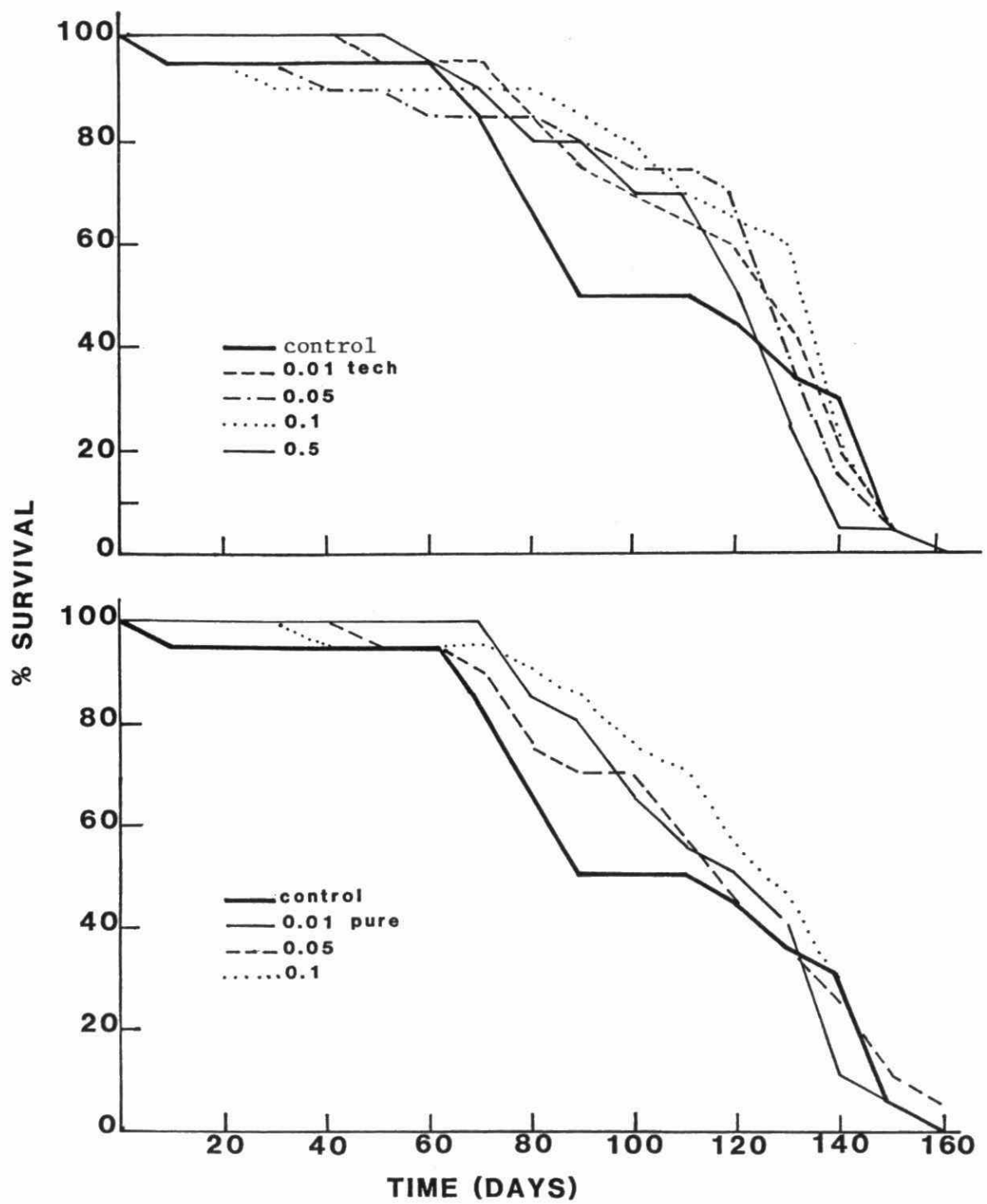


Fig. 1. Longevity of control daphnids and those exposed to technical and pure pentachlorophenol.

respectively. Thus the toxicity of both formulations of PCP appears to be more toxic at lower pH values. The trend appears to be similar for D.g. mendoate but a sample size of two is only indicative of a trend.

Table 8. Average number of young per brood per treatment (brood size).

Criterion 5		Concentration				
		0	0.01	0.05	0.1	0.5
Control	\bar{x}	11.29	-	-	-	-
	SD	4.39				
Technical PCP	\bar{x}	-	10.54	11.36	11.23	9.19
	SD		3.88	4.84	4.58	3.62
Pure PCP	\bar{x}	-	10.03	10.35	10.29	-
	SD		4.67	4.86	4.73	

DISCUSSION

Earlier studies, as summarized by Jones (1980), have recorded 24 LC₅₀ for Daphnia magna to range from 1.1 to 2.0 and 48-h LC₅₀ from 0.60 to 0.79 mg PCP/L. The values obtained in our studies for 24 to 72 h LC₅₀ ranged between 1.15 to 3.91 mg/L.

Exposure of D. magna to sublethal concentrations (ranging from 10 to 500 ug/L) of technical and pure PCP did not affect longevity. However, in a recent study (Hedtke et al. 1986) with three species of Cladocera (Ceriodaphnia reticulata, Simocephalus vetulus and Ceriodaphnia affinis), although most of the concentrations used (22 to 504 ug/L) did not affect survival, concentrations higher than 119 ug/L PCP did affect survival. However, these studies were carried out at pH 7.3 whereas the pH of well-water

used in our studies ranged between 7.5 to 7.8. Our preliminary studies indicate that water pH has a profound effect on toxicity and hence perhaps survival. The mean 48-h LC_{50} for adult D. magna at pH 7.8 for technical and pure PCP were 2.79 and 1.78 mg PCP/L, whereas corresponding values at pH 5.5 were only 0.88 and 0.58 mg PCP/L. So the effect observed by Hedtke et al. (1986) could be because of slightly lower pH value of water used by them. However, it is possible that the effect noticed by Hedtke et al. (1986) is because of the species of cladocera used. As observed with survival, Hedtke et al. (1986) did record significant effect on the number of young produced per female. In our studies no significant effect was observed in this regard also. These differences again could be because of the pH differences or because of different species of cladocera used as test organisms. They made no observations on the time to first brood and number of broods produced per female.

Acknowledgements

The authors are thankful to the Ontario Ministry of the Environment for financial assistance.

References

- Adelman, I.R. and L.L. Smith, Jr. 1976. Fathead minnows, Pimephales promelas and goldfish, Carassius auratus, as standard fish in bioassays and their reaction to potential reference toxicants. J. Fish. Res. Bd. Canada 33: 209-214.
- Cirelli, D.P. 1978. Patterns of pentachlorophenol usage in the United States of America - an overview. pp 13-18. In: K.R. Rao (ed.). Pentachlorophenol. Plenum Press, New York, NY.
- Enigk, K. and D. Duwel. 1960. Die Durchfuehrung der Bekampfung der Leberegelschmecke Galba truncatula (Limnaeidae) Monatsh. Tierheik. 12: 259.

- Fox, M.E. and S.R. Joshi. 1984. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. J. Great Lakes Research 10: 190-196.
- Gelfaud, M. 1941. Sodium pentachlorophenate treatment on cooling water. (Water Pollut. Abst. 14) Power Plant Eng. 45: 60.
- Guo, P.H.M., P.J.A. Fowlie, V.W. Cairns, and B.E. Jank. 1979. Activated sludge treatment of a wood preserving effluent containing pentachlorophenol. Wastewater Technology Centre E.P.S. Report.
- Hedtke, S.F., C.W. West, K.N. Allen, T.J. Norberg-King, and D.I. Mount. 1986. Toxicity of pentachlorophenol to aquatic organisms under naturally varying and controlled environmental conditions. Env. Tox. and Chem. 5: 531-542.
- Hoos, R.A.W. 1978. Patterns of pentachlorophenol usage in Canada - an overview. pp 3-13. In: K.R. Rao (ed.). Pentachlorophenol. Plenum Press, New York, NY.
- Inglis, A. and E.L. Davis. 1972. Effects of water hardness on the toxicity of several organic and inorganic herbicides to fish. U.S. Bureau Sport Fish. Wildlife Tech. Paper 67: 1-22.
- Jones, P.A. 1981. Chlorophenols and their impurities in the Canadian environment. Economic and Technical Review. EPS Report 3-EC-81-2. 434 pp.
- Mattson, V.R., J.W. Arthur, and C.T. Walbridge. 1976. Acute toxicity of selected organic compounds to fathead minnows. Environ. Res. Lab. U.S.E.P.A. Rept. No. EPA/600/3-76/097. PB-262 897.
- Palmer, C.M. and T.E. Maloney. 1955. Preliminary screening for potential algicides. Ohio J. Sc. 55(1): 1-8.

TOWARD THE DEVELOPMENT OF A STANDARD CLAM BIOMONITORING METHODOLOGY: PRELIMINARY RESULTS

E. Creese, D. Lewis & A. Melkic
Integrated Explorations
Guelph, Ontario

Introduction

The ability of organisms to accumulate environmental contaminants such as organochlorine compounds and heavy metals, has lead to their use in biomonitoring studies. Bivalve mollusks have been used in particular, especially in saltwater environments (Phillips, 1980). The popularity of bivalves stems from the fact that they are sedentary and thus represent the habitat in which they are found. An innovation which is still not widely practiced is the introduction of uncontaminated bivalves into habitats which are under investigation. The Ontario Ministry of the Environment (MOE) has been involved in this kind of study since the work by Curry (1977/78), who pioneered the use of the freshwater clam, *Elliptio complanata*, in the MOE.

Over the past several years in Ontario, the MOE and Environment Canada have conducted many biomonitoring studies using *E. complanata*, such as for example Kauss *et alia* (1981) and Kauss (1983). Integrated Explorations has been involved with many of these, including studies in the Niagara, St. Clair and St. Mary's Rivers and in Port Hope Harbour. Due to our involvement, particularly with the implimentation of these studies in the field, a number of questions have been brought into focus.

There are two primary areas of concern. The first is the availability of clams. To date, the source of *E. complanata* has been one area of one lake (Balsam Lake in the Kawartha district). Three hundred to thirteen hundred clams of this species in the size range 6.5 to 7.2 cm have been removed for Balsam Lake each year from 1980 to 1985 inclusive. We wanted to know if this is a reliable source. How large is the population and can it absorb the effects of government biomonitoring programs? Are there other easily reached sources of *E. complanata* or perhaps other species of clam that could be used in the event that the Balsam Lake population became contaminated? It was decided that finding such populations in areas diverse in terms of water pH and hardness would also prove useful.

The second area of concern is the tolerance of clams to field methods used during biomonitoring studies. Present field methods involve transporting the clams to the monitoring area, deploying them at the required sites and processing the clams after recovering them.

No standard method of transportation has been employed to date. Clams are maintained in Balsam Lake water. Gross overheating has been avoided by introducing ice into coolers if ambient temperatures are higher than that of Balsam Lake. Oxygen levels are checked occasionally, however, this is not a standard practice. To ensure adequate oxygen levels, large amounts of water are used to transport the clams. This method of transport has been used regardless of the distance of transport. An effort has been made to deploy the clams within a 24 hours of collecting them, however logistical problems have often caused variation in this period. Effects on bioaccumulation of differences in temperature, pH or current between Balsam Lake and the monitoring sites, although these parameters are recorded, are unknown. With current deployment methods, normal clam behaviour is interfered with. Clams can not assume their normal syphoning attitude with head down half buried in substrate. Clams in floating cages must endure very unnatural conditions. Do these deployment conditions lead to measurable effects on bioaccumulation?

Clams are usually deployed at the site in small flat rectangular galvanized steel mesh cages, as many as 17 clams per 30 cm square cage. The cages are tethered to some stationary object on shore to allow surface recovery. SCUBA has been used on occasion if surface recovery has been unsuccessful. A mid-depth cage is often suspended from the weighted bottom cage. Depth of cage deployment has varied from 2 m to greater than 10 m.

Processing methods to this point have been quite variable. Clams are usually shucked and frozen on dry ice on site, however, for various reasons, this is often not practical. At times clams have been kept on ice after shucking on site or clams have been kept alive on ice for varying periods after recovery before shucking and freezing.

After processing, analysis of clam tissues for various contaminants has been carried out at the Rexdale laboratory of the MOE. Currently 3 to 5 clams are analysed for each biomonitoring site.

Methods

Population Surveys

Balsam Lake

An intensive survey of the clam bed at Rosedale was carried out as well as a more extensive survey of other parts of Balsam Lake.

The Rosedale clam bed was defined in this survey as in Figure 1. It encompassed an area bounded on the south by the Trent Canal system channel, on the east by the shoreline of Balsam Lake on the west by the depth at which clams could no longer be found and on the north somewhat arbitrarily.

Observations of clams were made by a diver being towed by a boat. The transect lines which were used are shown in Figure 2. Communications between the diver and surface personnel enabled recording of the diver's observations on a map of the study area. Since it was impossible for the diver to actually count clams as he was passing over them, a clam density code was established by preliminary sampling. This code is presented in Table 1.

Table 1. Clam Density Terminology

<u>Description</u>	<u>Density Code</u>	<u>Mean</u>
Abundant	3	75/m ²
Frequent	2	15/m ²
Scarce	1	3/m ²
Absent	0	0/m ²

Size distribution of *E. complanata* in this bed was also investigated. Two areas of the bed were sampled. These two areas, Site A and Site B, are shown in Figure 2. Randomly chosen sample quadrats, of 1 m² size, picked clean of clams. Five quadrats were chosen at site A, an area thought to be relatively unexploited and seven were sampled at site B, an area known to have been used extensively as a source of clams for biomonitoring. For each quadrat, the number of *E. complanata* of each length were recorded.

Other areas of Balsam Lake were explored. Using the fact that *E. complanata* appeared to be restricted to depths

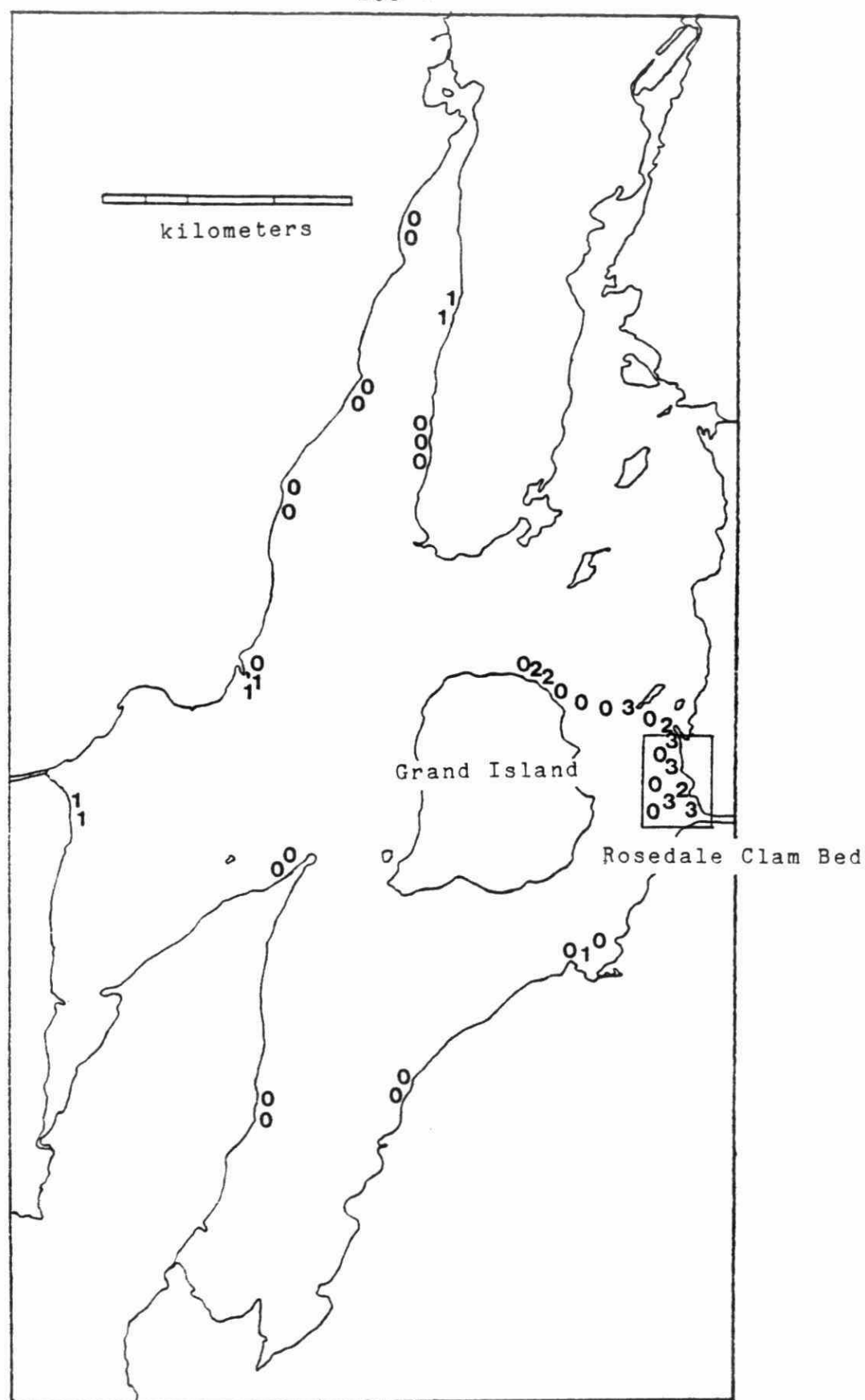


Figure 1. Map of Balsam Lake showing areas where population survey transects were run. Numbers refer to clam densities (see Table 1). The area inclosed in the rectangle is the Rosedale Clam Bed.

Scale: 1/6000

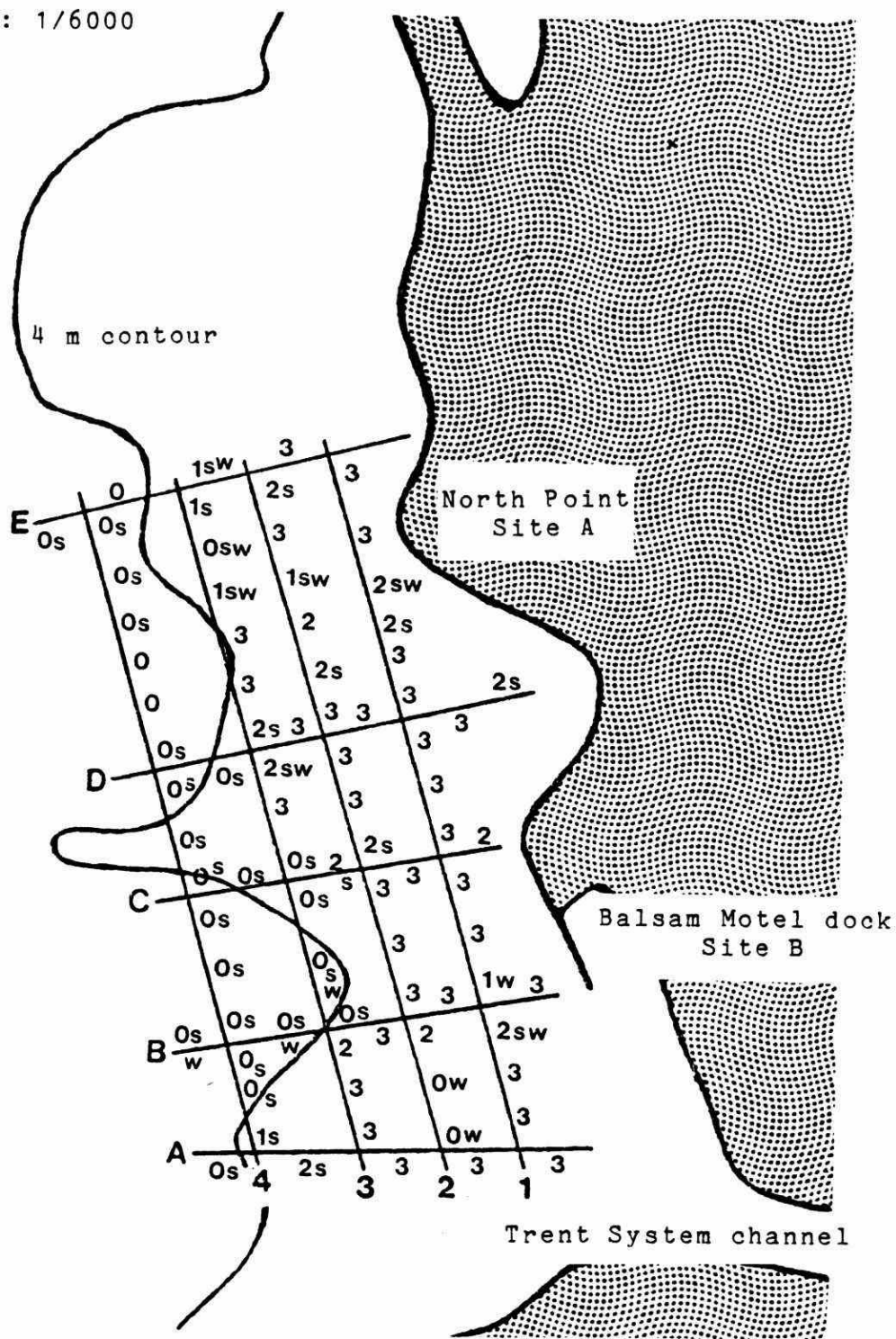


Figure 2. Map of the Rosedale Clam Bed area. The straight lines represent survey transects. Numbers are clam density codes (see Table 1). 's' indicates sand and/or silt and 'w' represents aquatic weeds.

of 4 m or less in the Rosedale clam bed, the area of exploration was similarly restricted for the most part. Transects therefore were run mostly at various places along the perimeter of the lake. One long transect that extended from the eastern shore of the lake to the northern most tip of Grand Island was also run. This transect took in a variety of substrates and included depths up to 7 m.

Other Lakes

In addition, other lakes in the area are to be investigated to find other exploitable clam populations. It was decided that finding such populations in areas diverse in terms of pH and hardness would also prove useful. Because the choice of *E. complanata* for biomonitoring seemed to be one of convenience, large populations of alternate clam species will also be noted.

As yet exploration of other lakes in the area for alternate sources of biomonitoring clams has not been carried out. This work will have been completed in November of 1986.

Experiments

The experimental part of this work has been established at a site at Niagara-on-the-Lake. The experiments have made use of Niagara River water as a source of contaminants which it is known that clams can accumulate. The experiments were concerned with the effect of various treatments on the uptake of contaminants. An examination of data on bioaccumulation in introduced clams in the Niagara River in 1980 and 1981 (Niagara River Toxics Committee, 1984) led to the conclusion that the only contaminant consistently present in concentrations above the detection limit, at Niagara-on-the-Lake, were PCB's. Therefore only differences in PCB concentrations in clams will be used in determining the effect of the various experimental treatments.

Effect of Temperature

A system was used that delivered Niagara River water into a series of temperature controlled tanks. A schematic diagram of the system is shown in Figure 3. Clams obtained from the Rosedale clam bed were exposed in a flow-through system at five temperatures, (5 C, 10 C, 15 C, 20 C and 25 C). An achievable flow rate, given the need for heating and cooling of river water for this system was 4 L/hr in each tank.

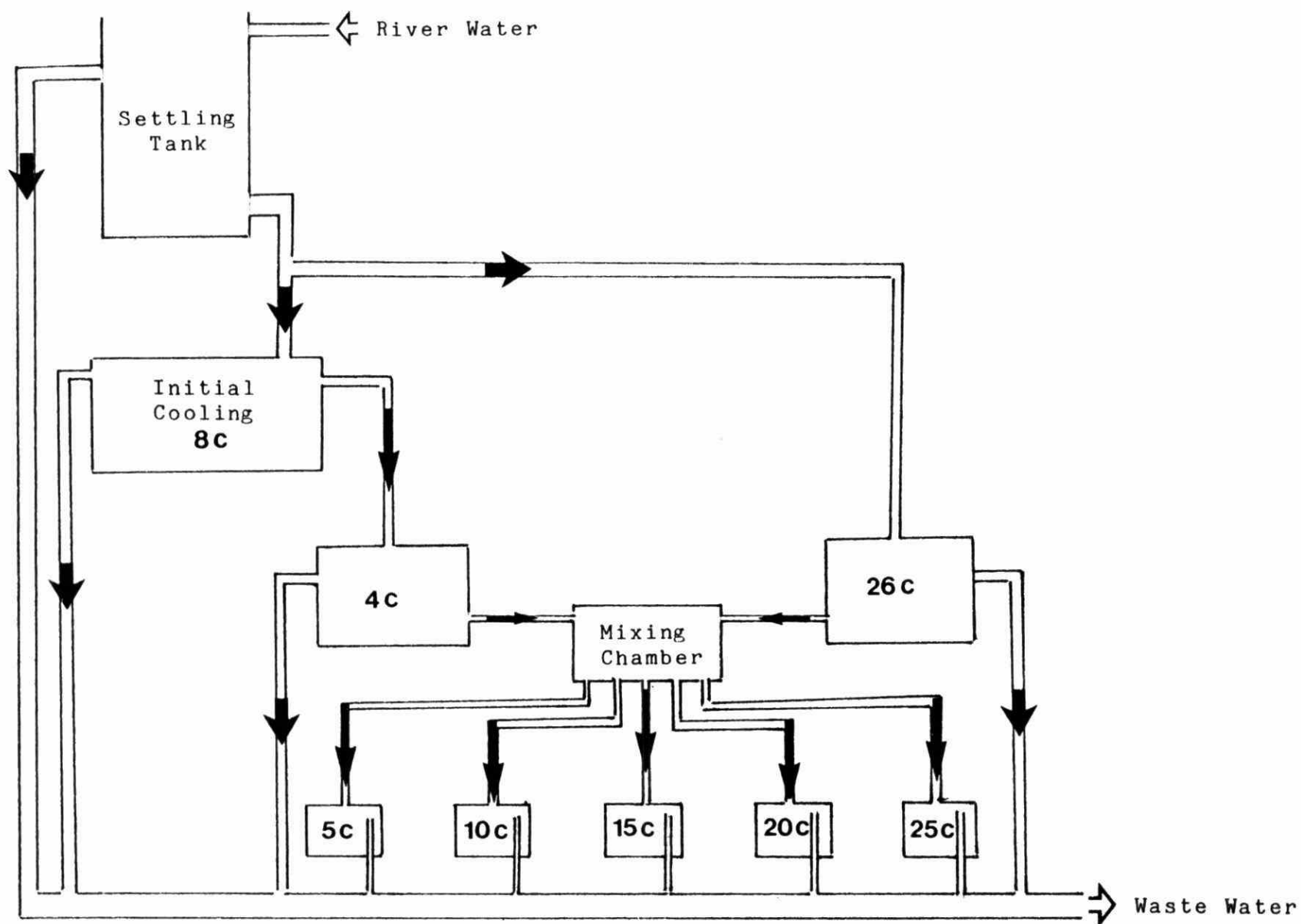


fig.3 Schematic of flow through system used in temperature test.

Prior to setting up the experiment, a check was made as to whether oxygen in incoming water would be sufficient for the needs of the clams. This was important since clams are known to reduce their filtration rates at low oxygen concentrations. For example, Badman (1974) found that **Pleurobema coccineum** had two activity regimes, one with active filtering in aerobic conditions and one with valves mostly closed in hypoxic conditions. It is likely that reduced filtration would lead to reduced bioaccumulation. The worst case was considered, one where the river water was very warm (25 C) and thus had a low oxygen concentration. It was assumed that the river water would, be saturated with oxygen since this has been noted from our past experience with the river. The saturation concentration at 25 C is 8.3 mg/L, which would give an oxygen flow rate in each of the five test aquaria, of 33 mg/hr if the incoming water was the sole source of oxygen. Each test tank contains twelve clams which would, at 20 C, use 3.0 mg/hr during sustained filtering or 4.2 mg/hr at peak oxygen consumption. These figures were arrived at using data on **Anodonta cygnea** cited by Imlay (1968). This consumption would lower the oxygen concentration from 8.3 mg/L to 7.3 mg/L. Even given some uncertainty of our estimate of clam oxygen consumption it seems unlikely that oxygen will be limiting the activity of our experimental clams even at 25 C.

Clams were exposed to this regime for a period of twenty one days, the period of time used for many biomonitoring studies. The clams were shucked immediately upon collection and frozen on dry ice. Frequent behavioural observations were made to augment chemical data.

The effect of acclimating clams to the various temperatures was also examined in this experiment by allowing half of the test clams to acclimate over a period of forty-eight hours before being exposed with the remaining clams to Niagara River water.

Effect of Biomonitoring Methods

Transport

Four transportation methods were investigated. Two methods had clams contained with large amounts of Balsam Lake water, one with the temperature controlled to equal the current temperature of Balsam Lake while the other was allowed to fluctuate with ambient temperature. In the two

other treatments clams were kept moist, one was allowed to fluctuate with ambient temperature while the other was kept cool on ice. All clams were obtained from Balsam Lake and kept under these conditions for forty-eight hours before deployment in the Niagara River.

Deployment

Presently clams are deployed in flat wire cages. No attempt has been made to simulate orientation or positioning of syphoning clams observed in their natural state. Syphoning clams have been observed to orient themselves syphon up. They achieve this position either by partially burying themselves in soft sediments or by wedging themselves between small rocks. Clam abundance in our experience is usually greatest in substrates that allow either of these two activities.

To establish whether the method of containment can effect clam PCB uptake, a series of containment devices were tested. Clams were deployed in the Niagara River using five different deployment treatments on a platform constructed by SCUBA divers and located in about 3 m of water. The intake for our flow-through temperature experiment was also located on this platform.

Three of the treatments used modifications of the present clam cages. One of these used a small version of the standard clam cage where clams were crowded together with little chance of orienting themselves in an upright position. Another cage kept clams from congregating but again prevented orientation. The third cage was a floating cage which suspended the clams in individual pockets at mid-depth in the water column. The fourth device consisted of a series of support rings 2.5 in. high and 2 in. diameter which held each clam in an upright position with syphons extended beyond the upper limit of the ring. Finally, small sand filled boxes containing large 5 in. diameter rings allowed the clams to orient themselves while preventing congregation.

Each method of deployment was combined with the four transport methods giving a treatment schedule as seen in Table 2.

Processing

The clams involved in the transport and deployment experiments were shucked immediately upon collection and

<u>Transport Methods</u>	<u>Deployment Methods</u>				
	Floating Cage	Compact Cage	Modified Standard Cage	Sand Box	Support Rings
Lake Temp. Wet	6	6	6	6	6
Ambient Temp. Wet	6	6	6	6	6
Ambient Temp. Moist	6	6	6	6	6
Ice Temp. Moist	6	6	6	6	6

Table 2. Transport and Deployment Treatment Schedule for 21 day Niagara River exposure, indicating numbers of clams included for each treatment.

frozen on dry ice.

Another series of clams, deployed on the underwater platform in support rings also for 21 days were involved in a processing test. The effect of various processing methods on bioaccumulation efficiency was investigated.

Five treatments have been carried out on these clams. Two groups were held on ice, for one hour and eight hours, before being shucked and frozen. Two groups were held at ambient temperature for one and eight hours, before being shucked and frozen. The final group was shucked immediately and quickly frozen in liquid nitrogen.

A minimum of three clams will be analysed for each experimental treatment. This number is in line with methods used by MOE for their biomonitoring activities. Information obtained from Mr. Peter Kauss of the Water Resources Branch indicates that due to variability between clams this level of analysis will allow detection of two- to three-fold differences in concentrations of PCB's.

It seems likely from the literature (Phillips, 1980) that increased precision in comparing treatments could be obtained by using lipid content of the clams as a covariate in analysis of variance. This possibility is presently being investigated.

Results and Discussion

Population Surveys

Balsam Lake

The results of the survey of the Rosedale clam bed can be seen in Figure 2. What the results indicate is that clams are abundant everywhere that the substrate consists of small stones and sand. Densities were lower when the bottom consisted solely of sand or silt especially if weeds were present. Clam densities declined rather abruptly at a depth of 4 m even on favorable substrates.

The mean densities corresponding to the density codes and the number of occurrences of each code within the clam bed were used to calculate a log-mean clam density for the entire bed of approximately 23/m². From navigational charts, the area of the Rosedale clam bed was calculated to be about 16 ha. The total population of the clam bed is therefore

^eestimated to be 3.7 million.

The average loss per year due to biomonitoring activities is 850 individuals ranging from 6.5 to 7.2 cm in length. From our observations during participation in this program, all clams harvested are of breeding age. This implies an indirect loss due to reduction of recruitment. The exact size of the breeding population is not known but for the purpose of this study is taken to include all clams 6.5 cm or greater. The results of our size distribution study indicate that this gives a total breeding population of 1.3 million. Although the size of the young of the year is not known we have taken it to be not greater than 2 cm. Using these assumptions, the average direct reduction in breeding population is therefore 0.07%. Although it is likely that larger individuals will produce more offspring than smaller individuals, we have made the conservative assumption that the annual recruitment rate will suffer a similar 0.07% reduction. Therefore the reduction in recruitment annually is estimated at 74 clams or less.

It can be seen from these calculations that the total expected population loss due to biomonitoring activities is not more than 1000 individuals per year on average. This reduction is thought to be insignificant when compared to the total population of close to 4 million. The loss is probably self-correcting due to the decrease in competition for available resources, allowing an increase in growth rate and therefore an increase in reproduction for the bed.

In other areas of Balsam Lake, the results of our survey indicate that it should not be expected to provide an alternate source of clams for biomonitoring. Population densities in other areas of the lake which were investigated proved too sparse to permit easy collection. This can be seen in Figure 1. An area immediately to the north of Grand Island had a small bed but this was not considered substantial enough to support long term biomonitoring efforts.

Experiments

Since the chemical analyses of the clam tissues are not yet completed, full experimental results can not be given.

Effect of Temperature

Observations of clams at the five test temperatures were

made throughout the 21 day trial. A gradient of clam activities was observed. Clams situated in the 15 C to 25 C tanks all showed active syphoning along with foot movement. Clams were so active that support rings had to be secured to prevent movement. Clams in the 10 C test tank also showed syphoning activity, however valve or foot movement was not noticed. Clams located in the 5 C tank were least active, showing reduced syphoning, valve closure and no foot movement.

As previously mentioned, reduced syphoning may lead to reduced bioaccumulation. At this point speculation leads us to believe that levels of PCB's in clam tissues will be reduced at lower temperatures, however this remains to be seen.

Effect of Biomonitoring Methods

No results are available at the present time.

Conclusions

- 1) The effect of harvesting clams for biomonitoring studies from the Rosedale clam bed in Balsam Lake is insignificant.
- 2) Other parts of Balsam Lake should do not represent an alternate source of clams for biomonitoring, since population densities are too sparse to permit easy collecting.
- 3) It appears from behavioural observations that temperature and deployment methods should be of concern for biomonitoring activities. More will be known when the results of the chemical analyses are available.

References

- Badman, D.G. 1974. Changes in activity in a freshwater clam in response to oxygen concentration. Comp. Biochem. Physio. 47A: 1265-1271.
- Curry, C.A. 1977/78. The freshwater clam (*Elliptio complanatus*), a practical tool for monitoring water quality. Water Pollution Research Canada, 13: 45-52.
- Imlay, M.J. 1968. Environmental factors in activity rhythms of the freshwater clam *Elliptio complanatus catawbensis*(Lea).

The American Midland Naturalist **80**: 508-528.

Kauss, P.B. 1983. Studies of trace contaminants, nutrients, and bacteria levels in the Niagara River. Journal of Great Lakes Research, **9**: 249-273.

Kauss, P.B., Griffiths, M. and Melkic, A. 1981. Use of freshwater clams in monitoring trace contaminant source areas. Conference Proceedings, Technology Transfer Conference No. 2, pp. 371-388. Research Advisory Committee, Ministry of the Environment, Province of Ontario.

Niagara River Toxics Committee, Report of. 1984.

Phillips, D.J.H. 1980. Quantitative Aquatic Biological Indicators. their use to monitor trace metal and organochlorine pollution. Appl. Sci. Publ., London.

EVALUATION OF DATA ON THE EFFECTS OF
HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION
ON RECEIVING WATER MICRO-ORGANISM DENSITIES

by

Dr. T.P.H. Gowda and Dr. M.D. Palmer
Gore & Storrie

EVALUATION OF DATA ON THE EFFECTS OF
HYDRAULIC CHARACTERISTICS AND EFFLUENT CHLORINATION
ON RECEIVING WATER MICRO-ORGANISM DENSITIES

ABSTRACT

Measured receiving water pathogenic bacterial densities downstream of treatment plant discharges were measured for both effluent disinfection and NO disinfection. A "plug" flow model predicted the receiving water densities within 0.5 log downstream of the Ingersoll (Thames River), Grand Valley (Grand River) and Peterborough (Otonabee River) WPCPs. provided the model was applied to each site separately for the day of sampling using a bacterial decay rate of 1.0/day (20°C, base e). Effluent disinfection reduced the receiving water bacterial degradations at each site. There were no statistical correlations between pathogens and indicator bacterial densities on the Thames and Grand Rivers. Klebsiella/total coliform, Pseudomonas aeruginosa/fecal coliform and Klebsiella/fecal coliform correlations did exist on the Ontonabee River for some density ranges.

1. INTRODUCTION

Chlorine disinfection of water has been a standard and widely accepted practice since the beginning of our century. Although this method of treatment has been remarkably effective in controlling waterborne bacterial diseases, the chlorine disinfection can produce small quantities of toxic trace organics like THM and residual chlorine in a receiving water is toxic to organism like fish and plankton (water quality objective is 2 ugm/L).

The Internal Joint Commission has proposed a residual chlorine water quality objective which would require treatment plants to dechlorinate effluents or apply alternative forms of disinfection. The dechlorination process increases the cost of treatment consequently the best solution would be not to disinfect at all, or at certain times, if the die-off of pathogenic bacteria could be left to natural conditions with assurance that it could not affect public health.

In 1979 the Ontario Ministry of the Environment selected Beak Consultants Limited (BEAK) to carry out a study investigating hydraulic, water quality and atmospheric conditions which contribute to the die-off bacteria from chlorinated and non-chlorinated sewage effluents in receiving waters. The overall objectives of the study were as follows (BEAK, 1982):

1. To determine if sewage effluents significantly contribute pathogenic bacteria and indicator bacteria to their receiving streams, during periods with sewage chlorination, and without;
2. To investigate the effects of natural assimilative capacity and hydraulic characteristics of the receiving waters on the growth and/or death rates of selected micro-organisms of public health importance;
3. To determine the relationship between the incidence of pathogenic bacteria and indicator bacteria in sewage effluents and in receiving waters, both with sewage chlorination and without;
4. To investigate the feasibility of using selected pathogenic bacteria as indicators of conditions hazardous to public health in effluents and receiving waters.

Detailed field studies as well as some preliminary data analyses and interpretations were carried out by BEAK Consultants Limited during 1979-82. The BEAK studies emphasized field data gathering for meeting the above objectives. The receiving water and Water Pollution Control Plant (WPCP) sites included in

the studies were as follows:

- Thames River - Ingersoll WPCP
- Grand River - Grand Valley WPCP
- Otonabee River - Peterborough WPCP
- Lake Ontario - Port Hope WPCP

All four WPCP's utilize conventional activated sludge treatment and chemical addition for nutrient reduction.

The data gathered in the BEAK study included bacteriological, chemical, hydraulic, hydrologic and meteorological characteristics from each of the four sites located in Southern Ontario. The final technical report prepared by BEAK Consultants Limited included the raw data collected in the study. The analyses which utilized somewhat simpler methods, were limited to a portion of the data gathered.

In 1982 Gore & Storrie Limited were retained by the Ontario Ministry of the Environment to carry out a follow-up study to analyze all pertinent data using acceptable mathematical methods. In following sections the objectives of the study and results obtained are presented.

2. OBJECTIVES OF THE STUDY

The objectives of the study were as follows:

1. To select mathematical models applicable to the study sites considering the dominant processes affecting bacterial transport (eg., advection, bacterial decay/regrowth, longitudinal and lateral dispersion); and to test the applicability of the selected models through comparisons of predictions with the BEAK study field data for each site.
2. To apply the selected models for determining the longitudinal and lateral distances (or travel times) with respect to the WPCP outfalls at which the total and fecal coliform densities are reduced to 1000/100 mL and 100/100 mL, respectively, for both chlorine disinfection and no-disinfection periods. The influence of seasonal change, receiving stream hydrological conditions and background bacterial concentrations are to be incorporated in this evaluation.
3. To establish the statistical relations of pathogenic bacteria concentrations in receiving streams when:
 - a) Total coliform concentrations in the same water were between 100 to 1000/100 mL or fecal coliform concentrations were between 10 to 100/100 mL;
 - b) Total coliform concentrations were between 1000 to 10,000/100 mL or fecal coliform concentrations between 100 to 1000/100 mL.

3. WATER QUALITY COMPLIANCE ZONES

3.1 General Approach

The selection and application of mathematical methods for the first two objectives are dependent on a number of factors. These include: (1) the ability of the models to simulate the dominant processes affecting bacterial transport in the receiving waters; (2) availability of data to determine the process parameters for the suitable models; (3) the desired level of accuracy; and (4) time-frame and other resource constraints.

In this chapter, the mathematical models suitable for the objectives 1 and 2 are outlined first by giving due consideration to the above-mentioned factors and the overall scope of the study. Then, the mathematical method applicable to each study site is outlined. The predictions are compared to the data collected by BEAK for each site. Finally, the predicted travel times at which the bacterial objectives are met, have been presented.

3.2 Description of Mathematical Methods

3.2.1 General Factors

The boundaries of bacteriological water quality compliance zones in the far field regions of rivers and lakes are dependent on the outfall characteristics, mixing of effluent in the receiving water, bacterial decay and regrowth processes, and steady/unsteady nature of the system. The models applicable to river and lake sites for defining water quality compliance zones are presented in the following subsections. These models are applicable to steady state conditions. Because of limitations imposed by time and resource constraints, and data availability, models for unsteady state conditions are not considered here.

3.2.2 Models for River Sites

All the three river sites studied by BEAK involved continuous discharge of effluents. However, the analyses presented by BEAK (1982) utilized the instantaneous discharges in an attempt to relate the effluent bacterial discharges to the observed instream bacterial data. Therefore, models applicable to both instantaneous and continuous discharge conditions are described herein.

3.2.2.1 Plug Flow Model - Continuous Discharge

If instantaneous complete mixing of effluent with the receiving water is achieved immediately below the outfall, then the one dimensional (1-D) plug flow model with first-order decay is applicable. This method has been applied to the Grand River below the Brantford WPCP (Post and Gowda, 1981). The mathematical relationships are presented below:

$$C_x = C_a \exp (-K_d X/U) \quad (1)$$

$$X_s = \frac{U}{K_d} \ln (C_a/C_s) \quad (2)$$

$$t_s = X_s/U \quad (3)$$

$$C_a = \frac{C_e Q_e + C_b Q_b}{Q_e + Q_b} \quad (4)$$

where C_e , Q_e = effluent bacterial density and flow rate, respectively

C_b , Q_b = background bacterial density and flow rate, respectively, in the river channel just above the outfall

K_d = decay rate of bacteria

U = average flow velocity in the river channel

X = distance below the outfall

C_x = concentration in the river at a distance, X , below the outfall

C_s = water quality objective

X_s = distance below the outfall at which the objective C_s , is met

t_s = travel time corresponding to X_s

The temperature dependence of K_d is expressed by the van't Hoff-Arrhenius relationship:

$$K_2 = K_1 \theta^{T_2 - T_1} \quad (5)$$

where K_1 and K_2 are the decay rates at $T_1^\circ\text{C}$ and $T_2^\circ\text{C}$, respectively; and θ is the temperature correction factor. The streamflow dependence of U is given by the

Leopold-Maddock relation:

$$U_2 = U_1 (Q_2/Q_1)^{u'} \quad (6)$$

where U_1 and U_2 denote velocities at the streamflow rates Q_1 and Q_2 , respectively; and u' is an exponent determined from field data.

3.2.2.2 Two-Dimensional Model - Continuous Discharge

If there are lateral concentration gradients in the far field region of the receiving stream, then a two dimensional (2-D) model that includes transport due to lateral dispersion and first-order decay should be utilized. The models applicable to such situations are described elsewhere (Gowda, 1980, 1984a and 1984b; Post & Gowda, 1981; Smith, et al, 1983; Putz, et al, 1984; Gowda & Post, 1984). The 2-D models developed from closed form analytical solutions are simpler to use. The models include MIXCALBN and MIXAPPLN for the case of pipe outfalls, and MIXCADIF for diffuser outfall discharges. The MIXCALBN and MIXCADIF models have been calibrated and verified using field data from rivers in Ontario (Gowda, 1980 and 1984b). The MIXCALBN and MIXAPPLN models are documented in a MOE publication (Gowda, 1980). The MIXCADIF model is quite similar to MIXCALBN with minor changes in input parameters.

3.2.2.3 Models for Instantaneous and Finite-Time Discharges

The mathematical methods applicable to these cases need to consider the advection and dispersion (longitudinal and/or lateral), and decay. Mathematical models for instantaneous and finite-time release cases are available (Gore & Storrie Ltd., 1984; 1985). However, the data presented in the BEAK report are not sufficient for such modelling studies. Therefore, these models are not considered further in this study.

3.2.3 Models for Lake Site

Mathematical models for coastal regions of lakes must account for transport due to longitudinal and lateral velocities and dispersion, as well as bacterial decay rates. Some of the models utilized by the MOE are described by Hamdy (1981) and Kohli (1981).

3. MATHEMATICAL MODELLING STUDIES

The analyses of mixing zone survey studies (September, November - December 1979, February 1980 for Thames River at Ingersoll; July - August, November 1979 for Grand River at Grand Valley; June, September - October 1980 for Otonabee River at Peterborough) showed that in the majority of cases analyzed, the plug flow model could be applied. In some cases the analyses showed that the models like MIXCALBN or MIXAPPLN would be more suitable. However, the lack of data necessary to calibrate and apply these models was the reason that the plug flow model was applied to these cases as well.

The lake study data for Lake Ontario at Port Hope were incomplete and no modelling is possible.

3.1 Thames River - Ingersoll WPCP

The daily average effluent flow rates were obtained from the plant operational records. The effluent bacterial densities measured on the survey days were gathered from the BEAK report.

The streamflow rates for the survey dates were obtained from the streamflow gauging stations located on Thames River at Ingersoll (upstream from the WPCP outfall) and Middle Thames River at Thamesford located below the WPCP. The study segment of the Thames River channel was divided into twelve reaches. The boundaries of these reaches include the sampling locations established in the BEAK studies. The streamflow values for the reaches lying between the outfall and the Middle Thames River confluence were calculated by adding the effluent and the upstream flow rates. For the reaches lying below the confluence, the Middle Thames River flow rates were added to those just above the confluence.

The average widths, depths and velocities for the reaches were estimated by utilizing the cross-sectional data presented in the BEAK Report in conjunction with the corresponding flow rate values. The Leopold-Maddock equations were utilized to adjust the widths, depths and velocities for the streamflow conditions observed during the surveys. These values are somewhat approximate estimates because of the fact that the exact dates of cross-sectional surveys and corresponding streamflows are not known.

The measured bacterial densities in the river just above the Ingersoll WPCP outfall were obtained from the BEAK Report. The river water temperature values observed during each survey were also obtained from the BEAK Report.

The plug flow model was utilized for this site. Individual modelling runs were carried out for each day of survey conditions. The decay rates (K_d) of fecal and total coliform bacteria were assumed to be 1.0 and 1.0 per day at 20°C (base e), respectively, for each reach based on the values reported in the literature (Zison, et al, 1978). These rates were adjusted to the temperatures observed on each sampling day (using Equation 5), and then applied to both the river background and effluent bacterial loadings.

For a comparison of the observations and plug flow model predictions, a factor (R_L) has been utilized. The factor is defined by:

$$R_L = \log \left(\frac{X_{\text{pred}}}{X_{\text{obs}}} \right)$$

in which X denotes the FC or TC bacterial density; and the subscripts "pred" and "obs" refer to the predicted and observed values, respectively. A positive value of R_L indicates a predicted value greater than observation and vice versa; and $R_L = 0$ implies perfect agreement of the two values. The bacterial measurement techniques are imprecise; and hence, the predicted and observed values are considered to be in reasonable agreement when the difference is within one-half log cycle, i.e. $R_L < \pm 0.5$.

The bacterial densities predicted by the plug flow model, as well as the measured densities for various sampling locations, are presented in Gore & Storrie 1986 for FC and TC, respectively. The times of travel (TOT) and R_L values are also given in the tables. The predicted and measured values are in reasonable agreement in most cases ($R_L < \pm 0.5$). For FC $R_L < \pm 0.5$ in 40 of 51 cases with Cl_2^- on and in 36 of 54 cases with Cl_2^- off. For TC the numbers are 37 of 51 and 37 of 54 respectively. Generally, the discrepancies are pronounced at the first station below the outfall and on those days when the background and/or effluent densities differed by more than two log cycles. The large discrepancies at the first station may be due to incomplete mixing (the model assumed complete mixing). In general, the differences seem to be unaffected by the seasons or travel times.

The plug flow model was utilized to determine the travel times with respect to the WPCP outfall at which the FC and TC densities are reduced to 100/100 mL and 1000/100 mL, respectively. The predicted travel times (hours) are summarized in Table 1 (See Appendix). In general, these predictions indicate that:

1. The travel times with effluent chlorination are generally much lower than those without effluent chlorination.
2. The river background densities have a significant effect on the travel times at which the desired objectives can be attained. Therefore, if upstream bacterial contamination is significant, then effluent disinfection may have very little effect on the stream bacteriological quality downstream of discharge.
3. The travel times are marginally affected by seasonal changes.

3.2 Grand River - Grand Valley WPCP Studies

The effluent, as well as river flow and quality data required for the plug flow model, were obtained from the plant operational data, streamflow records and the BEAK report. The decay rates for FC and TC bacteria were the same as for the Thames River studies (i.e., 1.0 and 1.0 per day) and were adjusted to the temperatures observed in the Grand River.

The observed and predicted FC and TC densities for various sampling runs are summarized in Gore & Storrie, 1986. As in the Thames River case, the predictions compare fairly well for some of the sampling runs and differ for others. For FC R_L is $< \pm 0.5$ in all cases (both for Cl_2 on and off). For TC R_L is $< \pm 0.5$ in 34 of 36 cases with Cl_2 - on and in 25 of 36 cases with Cl_2 - off. The differences between the observations and predictions are seen to be quite significant for the days when the upstream densities are considerably different from the other sampling days.

The travel times at which the FC and TC densities are reduced to the guideline values of 100/100 mL and 1000/100 mL, respectively, are presented in Table 2. These predictions by the plug flow model are seen to be lower with effluent chlorination compared to the non-chlorination runs. The observed changes in background densities from one day to another are seen to affect the travel time values. The findings herein are somewhat similar to the Thames River results.

3.3 Otonabee River - Peterborough WPCP Studies

The WPCP effluent quality and flow rates, as well as the Otonabee River characteristics, were determined from various sources as for the Thames and Grand River Studies. The bacterial decay rates were also the same as in the other river studies, scaled up to the average river temperatures for each sampling day.

The FC and TC densities predicted by the plug flow model for the Otonabee River sampling sites are presented in Gore & Storrie, (1986) along with the corresponding observed values. The predictions are closer to the observations for some sampling runs, but differ in others, as for the other two river study sites. For FC R_L is $< \pm 0.5$ in 24 of 30 cases with Cl_2 - on and in 18 of 29 cases with Cl_2 - off. The numbers for TC are 23 of 30 and 24 of 30 respectively. The observed background densities on different sampling dates affect the comparative results at this river site as well.

The plug flow model predictions of travel times at which the FC and TC densities are reduced to the guideline values have been summarized in Table 3. The trends of these travel times are generally similar to those of the Thames and Grand River values.

3.4 Sensitivity of Background Bacterial Densities

The model predictions for various river sites, presented in the previous section, indicated the significance of the background levels on the times of travel at which the water quality objectives are met. The analyses for each site were both without and with background bacterial densities. In order to further evaluate the sensitivity of the background levels, additional plug flow modelling studies were carried out for the Grand River site by assuming the following levels for the summer runs:

Background FC = 100/100 mL

Background TC = 1000/100 mL

These background levels are the same as the provincial water quality objectives (PWQO). The effluent densities, decay rates and other input parameters for the

model were the same as those observed during the summer 1979 Cl₂-ON (August 4 to 6) and Cl₂-OFF (August 12 to 14) studies.

The predicted travel times below the outfall at which the FC and TC bacterial objectives can be met, are summarized in Table 4. A comparison of these travel times with the corresponding values (predicted with the observed background levels) indicates that the maintenance of background levels at or lower than the PWQO will result in significant reductions in the travel times (particularly for the disinfected case) within which PWQO cannot be met. These sensitivity run predictions indicate that efforts should be directed at maintaining background bacterial densities at or below the PWQO levels.

3.5 Discussion

The discrepancies between the observations and predictions are in part caused by field sampling methodology, imprecise analytical measurement techniques, effects of ambient environmental factors, etc. Attempts were made to qualitatively assess the possible effects of sediment characteristics, hydraulic parameters and inorganic water quality parameters on the modelling results by utilizing the data presented in the BEAK report. An examination of the pertinent data for the successive reaches from each river site did not reveal any clearly identifiable factors to explain the discrepancies. However, the empirical method of using an error range (defined by the ratio $R_L < \pm 0.5$) to include most errors.

The plug flow model predictions compared reasonably well with observations with a few exceptions for each site. The assumed decay rates for FC and TC were satisfactory. Since all the river sites consist of shallow reaches, the assumed decay rates appear to be valid for the river reaches studied herein. These rates could be used for preliminary planning studies. However, their validity to a given site should be checked with the aid of field data and modelling studies.

4. STATISTICAL ANALYSIS

The total coliform (TC) and fecal coliform (FC) density data were correlated with Pseudomonas aeruginosa (PA) and Klebsiella (K). In the Beak report, the log (TC) and log (FC) were correlated with the log (PA) and log (K); however, the correlations were statistically not significant. These statistical correlations were repeated but the data were separated into groups for the river sites,

namely, the Grand, Thames and Otonabee Rivers. The statistical results are summarized in Table 5. For the Otonabee River, K with TC greater than 1000/100 mL and K with FC greater than 100/100 mL have correlation coefficients of 0.78 and 0.79, respectively. The correlation coefficients are not statistically significant for all other cases.

To determine whether better statistical correlations could be obtained, the data sets were partitioned. There is a low value bias of 4 counts/100 mL for PA in the data sets; consequently, a new data set was created, omitting all PA densities of 4 or less. It is also known that the FC density evaluation is imprecise. Data from the Eastern Beaches (Toronto waterfront) indicated a precision of $\log(\text{var})$ equal to 0.54 (N=1121) and the MOE data have indicated a precision of $\log(\text{var})$ equal to 0.7 for Lake Ontario (Gore & Storrie Limited, 1985). The 1986 data for Western Beaches had even greater values of $\log(\text{var})$ varied between 0.97 (N=1270) and 1.09 (N=686) for the samples taken inside and outside of breakwater respectively. Furthermore, the present guidelines for FC for receiving waters are that the geometric mean of 10 samples should not exceed 100/100 mL. The following table shows the upper limits for the FC geometric mean of 100/100 mL based on sample size, assuming a normally distributed population (U.S. Federal Register 49 (102); 21987, 24 May, 1984):

NO. OF SAMPLES	LOG (VAR) = 0.54	LOG (VAR) = 0.7
1	778	1429
2	427	655
5	250	329
10	191	232

The bacteriological sampling in the BEAK study involved one sample at each station. Therefore, instead of the interval 10 to 100/100 mL and 101 to 1000/100 mL for FC densities, the intervals of 0 to 777/100 mL and 778 to 7000/100 mL were used assuming a precision of $\log(\text{var}) = 0.54$. The results of the statistical fitting of this data set are presented in Table 6. This partitioning of the data set did not improve the statistical fitting for the Grand and Thames Rivers, however, it did produce statistically significant relationships for PA/FC for the Otonabee River data.

Tables 5 and 6 show that the correlations between TC/FC with PA/K are generally statistically not significant for the data sets, except for the Otonabee River data which has the following relationships:

OTONOBEE RIVER

1. TC = 1001 to 10,000/100 mL	$\log (K) = - 3.48 + 0.6 \log (TC)$
2. FC = 10 to 777/100 mL	$\log (PA) = 1.34 - 0.2 \log (FC)$ $\log (K) = 0.68 + 0.57 \log (FC)$
3. FC = 778 to 7000/100 mL	$\log (PA) = - 1.45 - 0.74 \log (FC)$ $\log (K) = 0.19 + 0.82 \log (FC)$

5. SUMMARY AND CONCLUSIONS

Data related to bacteriological impact of effluent discharges to water bodies were analyzed. The studies were conducted by BEAK Consultants Limited during 1979-82 at the following sites:

- Thames River - Ingersoll WPCP
- Grand River - Grand Valley WPCP
- Otonabee River - Peterborough WPCP
- Lake Ontario at Port Hope WPCP

The data review and analyses focussed on the following objectives:

1. Determination of longitudinal and lateral distances (or travel times) with respect to the WPCP outfalls at which the fecal and total coliform densities are reduced to 100/100 mL and 1000/100 mL respectively, for both chlorine disinfection and no-disinfection periods.
2. Establishment of statistical relationships distributions of pathogenic bacteria concentrations in receiving streams when:
 - a) Total coliform concentrations in the same water were between 100 to 1000/100 mL or fecal coliform concentrations were between 10 to 100/100 mL; and
 - b) Total coliform concentrations were between 1000 to 10,000/100 mL or fecal coliform concentrations between 100 to 1000/100/mL.

The suitability of data presented in the BEAK Report for applying the state-of-the-art models to each site was evaluated. It was found that 2-D models (capable of simulating transport due to lateral dispersion, longitudinal convection and decay) could not be utilized because data were not available. The lake study data were also insufficient for modelling.

The plug flow model was the most suitable model for the three river site analyses. The model was applied for each day of sampling, since the effluent and background loadings were different on each day. The bacterial decay rate was assumed to be 1.0/day (20° C, base e) for both TC and FC.

The plug flow model generally predicted observations within one half log cycle. The largest discrepancies occurred on days when the background levels differed significantly from the other days' values at the first station below the outfall. This was the case for each site. The travel times at which the TC and FC densities are reduced to the guideline limits (stated in the first objective) were smaller with effluent disinfection at each site compared to the non-disinfected cases. The background densities of FC and TC affect the travel time computations.

Statistical correlation analyses of pathogen and indicator bacterial densities were carried out. No correlation relationships could be found for the Thames and Grand River data. Only the Otonabee River bacterial data showed correlations between: (a) Klebsiella and TC; (b) P.aeruginosa and FC; and (c) Klebsiella and FC. These relationships are established for the ranges TC = 1001 to 10,000/100 mL, FC = 10 to 777/100 mL and FC = 778 to 7000/100 mL in order to account for imprecise evaluations of the bacterial densities.

REFERENCES

- Beak Consultants Ltd., 1982. Bacteria in Sewage Effluents - The Effects of Hydraulic Characteristics and Effluent Chlorination on the Incidence of Micro-Organisms of Public Health Significance in Receiving Waters. Technical report prepared for the Ministry of the Environment, Toronto, Ontario.
- Gore & Storrie Limited, 1986. Evaluation of Data on the Effects of Hydraulic Characteristics and Effluent Chlorination on the Incidence of Micro-organisms of Public Health Significance in Receiving Waters. Technical report prepared for the Ontario Ministry of the Environment.
- Gore & Storrie Limited, 1985. Eastern Beaches Study - 1984. Technical report prepared for the City of Toronto.
- Gore & Storrie Limited, 1984. Ottawa River Nuclear Spill Contingency Model Development. Technical Report prepared for the Ontario Ministry of the Environment, Toronto.
- Gowda, T.P.H., 1980. Stream Tube Model for Water Quality Prediction in Mixing Zones of Shallow Rivers. Water Resources Paper 14, Water Resources Branch, Ministry of the Environment, Toronto, Ontario, Canada. 141 p.
- Gowda, T.P.H., 1984a. Critical Point Method for Mixing Zones in Rivers. J. Environmental Engineering, Amer. Soc. Civ. Eng. 110 (1): 244 - 262.
- Gowda, T.P.H., 1984b. Water Quality Prediction in Mixing Zones of Rivers. J. Environmental Engineering, Amer. Soc. Civ. Eng. 110 (4): 751-769.
- Gowda, T.P.H. and Post, L.E., 1984. Mixing Zone Studies in the Grand River Basin. Canadian Journal of Civil Engineering 11 (2): 204-216.
- Hamdy, Y., 1981. Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes. Vol. I - Initial Mixing Processes. Great Lakes Section, Water Resources Branch, Ministry of the Environment, Toronto.
- Kohli, B., 1981. Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes. Vol. II - Surface Dilution. Great Lakes Section, Water Resources Branch, Ministry of the Environment, Toronto.
- Post, L.E. and Gowda, T.P.H., 1981. Effluent Mixing Zone Studies. Grand River Basin Water Management Study - Technical Report No. 29, Water Resources Branch, Ontario Ministry of the Environment, Toronto.
- Putz, G., et al, 1984. Micro-organism Survival in an Ice-Covered River. Canadian Journal of Civil Engineering 11 (2): 177-186.
- Smith, D.W., et al, 1983. Effluent Mixing in Northern Rivers - The Bank Discharge. Paper presented at the Chemical Institute of Canada Conference, Calgary, June 1983.
- Zison, S.W., et al, 1978. Rates, Constants and Kinetic Formulations in Surface Water Quality Modelling. Tetra Tech., Inc., Lafayette, California. Technical report prepared for the U.S.E.P.A. 317 p.

APPENDIX - TABLES

Table 1

SUMMARY OF PREDICTED TRAVEL TIMES WHERE BACTERIAL OBJECTIVES ARE MET - THAMES RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE FC OBJECTIVE = 100/100 mL		TRAVEL TIME (HRS) WHERE TC OBJECTIVE = 1000/100 mL		UPSTREAM RIVER DISCHARGE (m ³ /s)
		Without Background	With Background	Without Background	With Background	
<u>Summer</u>						
Sept. 6-8, 1979	Cl ₂ -ON:					
	Day 1	20.08	88.43	1.72	25.00	1.75
	Day 2	0.0	94.71	0.0	128.89	1.71
	Day 3	0.0	138.35	0.0	115.56	1.67
Sept. 19-21, 1979	Cl ₂ -OFF:					
	Day 4	200.96	202.13	142.15	148.03	1.85
	Day 5	158.58	163.09	142.37	149.99	1.76
	Day 6	158.41	158.86	216.99	217.47	1.87
<u>Fall</u>						
Nov.30 - Dec.2 1979	CL ₂ -ON:					
	Day 1	0.00	76.85	0.0	81.07	3.05
	Day 2	4.46	83.84	30.89	103.92	2.15
	Day 3	44.74	76.99	0.0	97.98	1.63
Dec. 10-12 1979	Cl ₂ -OFF:					
	Day 4	14.16	68.30	27.50	125.14	5.41
	Day 5	4.84	92.40	0.14	123.53	4.96
	Day 6	0.0	103.32	1.09	99.89	4.86
<u>Winter</u>						
Feb. 7-9 1980	Cl ₂ -ON:					
	Day 1	0.0	89.24	0.0	96.50	2.15
	Day 2	0.0	77.44	0.0	86.30	2.12
	Day 3	0.0	58.78	0.0	45.65	2.08
Feb. 19-21 1981	Cl ₂ -OFF:					
	Day 4	130.32	137.74	138.69	140.50	1.90
	Day 5	111.48	122.97	129.46	133.42	1.90
	Day 6	87.36	137.92	115.63	127.75	2.50

Table 2

SUMMARY OF PREDICTED TRAVEL TIMES WHERE BACTERIAL OBJECTIVES ARE MET - GRAND RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE FC OBJECTIVE = 100/100 mL		TRAVEL TIME (HRS) WHERE TC OBJECTIVE = 1000/100 mL		UPSTREAM RIVER DISCHARGE (m ³ /s)
		Without Background	With Background	Without Background	With Background	
<u>Summer</u>						
August 4-6, 1979	Cl ₂ -ON:					
	Day 1	0.0	29.1	0.0	59.7	0.5667
	Day 2	0.0	25.5	0.0	59.9	0.5306
	Day 3	0.0	0.0	0.0	44.6	0.4697
August 12-14, 1979	Cl ₂ -OFF:					
	Day 1	21.2	50.5	0.0	49.9	0.7398
	Day 2	28.3	48.6	0.0	48.5	0.6817
	Day 3	29.1	44.7	0.0	112.3	0.7449
<u>Fall</u>						
Nov. 5-7, 1979	CL ₂ -ON:					
	Day 1	0.0	0.0	0.0	3.6	3.7575
	Day 2	0.0	0.0	0.0	0.0	3.0578
	Day 3	0.0	36.2	0.0	0.0	3.0573
Dec. 16-18, 1979	Cl ₂ -OFF:					
	Day 1	0.0	86.5	0.0	11.4	3.1377
	Day 2	0.0	3.5	0.0	42.9	3.0477
	Day 3	0.0	17.1	0.0	0.0	3.3075

Table 3

SUMMARY OF PREDICTED TRAVEL TIMES WHERE BACTERIAL OBJECTIVES ARE MET - OTONABEE RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE FC OBJECTIVE = 100/100 mL		TRAVEL TIME (HRS) WHERE TC OBJECTIVE = 1000/100 mL		UPSTREAM RIVER DISCHARGE (m ³ /s)
		Without Background	With Background	Without Background	With Background	
<u>Summer</u>						
June 5-7, 1980	Cl ₂ -ON:					
	Day 1	0.0	14.6	0.0	22.0	37.90
	Day 2	0.0	30.9	0.0	20.2	21.20
	Day 3	0.0	4.6	0.0	28.7	21.10
June 16-18, 1980	Cl ₂ -OFF:					
	Day 1	112.6	112.9	87.8	90.0	23.00
	Day 2	78.9	80.3	63.7	65.6	20.30
	Day 3	104.1	104.9	89.1	89.5	23.50 ¹
<u>Fall</u>						
Sept. 30 - Oct. 2, 1980	CL ₂ -ON:					
	Day 1	0.0	3.0	0.0	2.5	34.10
	Day 2	0.0	7.0	0.0	0.0	34.50
	Day 3	0.0	0.0	0.0	0.0	39.00
Oct. 14-16, 1980	Cl ₂ -OFF:					
	Day 1	92.2	92.8	10.1	27.5	46.80
	Day 2	50.0	51.8	41.8	53.2	46.60
	Day 3	33.4	42.6	19.0	36.9	50.40

240 -

Table 4

SENSITIVITY OF BACKGROUND LEVELS ON PREDICTED TRAVEL TIMES
GRAND RIVER

SEASON & DATE	CASE	TRAVEL TIME (HRS) WHERE OBJECTIVES ARE MET	
		With FC Background = 100/100 mL	With TC Background = 1000/100 mL
<u>Summer</u>			
August 4-6, 1979	Cl ₂ -ON:		
	Day 1	0.03	0.08
	Day 2	0.0	0.0
	Day 3	0.0	0.0
August 12-14, 1979	Cl ₂ -OFF:		
	Day 1	28.6	13.3
	Day 2	34.0	13.8
	Day 3	34.6	9.6

Table 5

	TOTAL COLIFORMS (Counts/100 mL)		FECAL COLIFORMS (Counts/100 mL)	
	100 to 1000	1001 to 10000	10 to 100	101 to 1000
<u>PSEUDOMONAS AERUGINOSA</u>				
<u>Grand River</u>				
Number of readings	21	41	25	57
Intercept	0.63	- 1.60	0.55	- 0.19
Slope	- 0.0056	0.72	0.18	0.42
Correlation coefficient	- 0.0042	0.40	0.08	0.25
<u>Thames River</u>				
Number of readings	2	57	2	81
Intercept	--	1.79	--	- 0.02
Slope	--	- 0.21	--	0.37
Correlation coefficient	--	- 0.14	--	0.19
<u>Otonabee River</u>				
Number of readings	17	64	28	44
Intercept	- 0.74	- 1.18	0.60	- 0.15
Slope	0.38	0.45	- 0.20	0.21
Correlation coefficient	0.20	0.40	- 0.15	0.24
<u>KLEBSIELLA</u>				
<u>Grand River</u>				
Number of readings	30	52	32	64
Intercept	1.62	2.95	1.81	2.35
Slope	0.20	- 0.23	0.14	- 0.10
Correlation coefficient	0.11	- 0.21	0.11	- 0.09
<u>Thames River</u>				
Number of readings	5	61	5	89
Intercept	2.15	2.40	0.28	1.01
Slope	0.12	0.01	1.03	0.51
Correlation coefficient	0.04	0.01	0.54	0.27
<u>Otonabee River</u>				
Number of readings	20	44	33	26
Intercept	0.40	- 3.48	1.11	- 0.33
Slope	0.47	0.61	0.32	0.99
Correlation coefficient	0.29	0.78	0.20	0.79

Slope assumes TC/FC are independent variables.

Correlation coefficient assumes both TC/FC and PA/K are dependent variables.

Table 6

		FECAL COLIFORMS	
		10 to 777	778 to 7000
GRAND RIVER			
<u>Pseudomonas aeruginosa</u>			
Number of readings	24	16	
Intercept	1.05	1.78	
Slope	0.19	- 0.13	
Correlation coefficient	0.17	- 0.09	
 <u>Klebsiella</u>			
Number of readings	86	29	
Intercept	1.98	- 1.05	
Slope	0.05	1.05	
Correlation coefficient	0.05	0.63	
 THAMES RIVER			
<u>Pseudomonas Aeruginosa</u>			
Number of readings	49	56	
Intercept	0.78	- 0.19	
Slope	0.11	0.48	
Correlation coefficient	0.08	0.28	
 <u>Klebsiella</u>			
Number of readings	77	67	
Intercept	1.06	2.17	
Slope	0.48	0.11	
Correlation coefficient	0.37	0.06	
 OTONABEE RIVER			
<u>Pseudomonas aeruginosa</u>			
Number of readings	7	25	
Intercept	1.34	- 1.45	
Slope	- 0.20	0.74	
Correlation coefficient	- 0.87	0.83	
 <u>Klebsiella</u>			
Number of readings	54	16	
Intercept	0.68	0.19	
Slope	0.57	0.82	
Correlation coefficient	0.56	0.88	

Listowel Artificial Marsh Treatment Project
J. Herskowitz, S. Black, W. Lewandowski¹

Abstract

Five separate cattail (*Typha* spp.) marsh treatment systems, occupying a total area of 8670 m², were operated for four years. Several different marsh designs and two pre-treatment types, namely, complete-mix aeration cell effluent and lagoon effluent from the existing Town of Listowel sewage works, were tested. Marsh effluent quality achieved was at levels between conventional secondary and tertiary treatment. The marsh systems demonstrated large reductions in BOD and suspended solids on a year-round basis. Elevated ammonia, hydrogen sulphide and phenol levels in the marsh effluent in summer and/or winter months were primarily attributed to anaerobic conditions, although low temperatures appeared to be a factor in decreased ammonia removal in winter. The observed decline in annual phosphorus retention suggests progressive saturation of the phosphorus adsorption capacity of the sediment. Large reductions in fecal bacteria were achieved although in some months levels exceeded Ministry objectives for disinfected effluent. Pilot study recommendations for marsh system design and operation have been implemented at a full-scale marsh treatment facility currently operated in Port Perry, Ontario.

Key words: wetlands, cattails, *Typha*, wastewater, municipal sewage.

Introduction

The study of marsh wastewater treatment systems was initiated by the Ontario Ministry of the Environment in response to reports that they may provide a viable and cost-effective alternative to conventional practices of wastewater treatment in rural communities and small urban centres. Many communities in Ontario use seasonal or annual retention lagoons which must be large enough to retain the wastewater until there is adequate dilution in the receiving waters to meet Ministry water quality guidelines (MOE, 1984). Marsh treatment has the advantages of

¹ Water Resources Branch, Ontario Ministry of Environment, 135 St. Clair Ave. W., Toronto, Ontario, Canada M4V 1P5

being less land consumptive than seasonal or annual retention lagoons and more economical and energy efficient than mechanical systems.

The primary objectives of the Listowel Artificial Marsh Project were 1) to investigate the efficiency and feasibility of year-round marshland wastewater treatment in cold climates and 2) to provide guidelines for the design and operation of marsh systems in Ontario. This paper describes the operating conditions and effluent quality achieved in Systems 3 and 4, channelized marshes used to treat lagoon effluent and aeration cell effluent, respectively, as the channelled design yielded the highest treatment efficiencies.

Description of Site and Facilities

The experimental facility was constructed adjacent to the existing 1.2 MIGD sewage works in the Town of Listowel and was operated from 1980 to 1984. A food processing plant with poultry handling facilities contributed 60-70% of the total sewage volume and BOD loadings. The existing sewage treatment at Listowel consisted of alum injection prior to a complete-mix aeration cell (3.5 day HDT) followed by two wastewater stabilization lagoons operated in series (combined retention 85 days). Alum treatment was withheld during the first two summers (May-Oct., 1981 and 1982) as the town spray irrigated an adjoining property in summer. The five separate experimental marsh systems treated 4% of the town's sewage. Wastewater was diverted from two stages of the existing system and distributed to the marsh systems as shown in Figure 1.

The marsh system designs included a channelized marsh with serpentine configuration (Systems 3 and 4), a shallow marsh (Systems 2 and 5) and a complex of shallow marsh, deep pond and channelized marsh (System 1). The channels, separated by earthen berms, were 4 m wide and 334 m long (length width ratio 17:1 in each channel). Surface areas of Systems 1 through 5 were 4172, 909, 1324, 1324 and 941 m², respectively. The marsh basins were composed of compacted clay and filled to a depth of 15 cm with a combination of top soil and peat (10% by volume). Cattails (predominantly Typha latifolia with some T. angustifolia present), propagated from rhizomes planted at 1 m intervals, provided a complete cover which was maintained throughout the study. The pilot project has been described in more detail in earlier reports (Wile et al, 1981; Black, 1983; Wile et al, 1985; Reed et al, 1985; Herskowitz, 1986).

Operational Conditions and Procedures

Wastewater from the existing lagoon and aeration cell was pumped to two flow splitting boxes and was then fed by gravity to the marsh systems. Inflows and outflows monitored by 30° v-notch weirs and water level recorders were used to calculate mass balances of wastewater constituents and treatment efficiencies. Due to computations indicating an excess of total hydrological input over output in some months (attributed to an underestimate of outflow discharge), monthly mass balances were adjusted accordingly to avoid overestimating treatment efficiencies.

Average hydraulic flow rates and loadings to the channelized systems were $17 \text{ m}^3 \text{ d}^{-1}$ (0.2 L sec^{-1}) and $128 \text{ m}^3 \text{ ha}^{-1} \text{ d}^{-1}$, respectively, for most of the study period. Hydraulic loadings were increased (2-3 times initial levels) during the first year (beginning in winter) to prevent freezing. As the higher loadings resulted in reduced treatment efficiencies, in the following winter culvert aerators and effluent chamber heaters were installed instead to prevent flow blockage from ice formation. Average influent BOD-5 concentrations and annual loadings (following the first year) were 20 mg L^{-1} (range $3\text{--}69 \text{ mg L}^{-1}$) and 86 g m^{-2} (range $74\text{--}100 \text{ g m}^{-2}$), respectively, in System 3 and 56 mg L^{-1} (range $10\text{--}168 \text{ mg L}^{-1}$) and 294 g m^{-2} (range $239\text{--}359 \text{ g m}^{-2}$), respectively, in System 4.

Theoretical retention times were altered by evapotranspiration, ice formation and precipitation. High rates of evapotranspiration in summer tended to increase the retention time causing stagnation and anoxia. In order to increase the rate of flow through the marshes in summer, the water depth was lowered to 5-20 cm. The presence of a 5 cm lip on the outflow chambers prevented the complete drainage of the marshes in summer and, therefore, precluded intermittent drying of the sediment, which would likely have increased the oxygen content of the sediment and contributed to greater contaminant removal in summer (Brinson, 1985). To maintain a water depth of 20 cm and counteract short-circuiting due to ice blockages, water levels were raised to ≥ 30 cm prior to the onset of winter. Heavy rains may have temporarily reduced the retention time but the resulting dilution tends to balance losses in treatment efficiency. Treatment efficiencies declined when retention time in the marshes deviated from the range of 7-14 days.

Monthly average temperatures of marsh effluents ranged between 0° and 19.6°C (daily temperatures as high as 26.5°C were measured in summer). In December through March, monthly average temperatures were consistently less than 2°C. Monthly average marsh effluent pH values generally fell within the range of 6.5-7.5 (measurements ranged between 6.3 and 8.9).

Routine chemical parameters and fecal indicator bacteria were monitored weekly from April to November and biweekly from December to March. Tests for hydrogen sulphide, phenols and bacterial pathogens were conducted predominantly in winter. Analytical techniques are described elsewhere (MOE, 1981).

Results and Discussion

1. Dissolved Oxygen Levels and Sediment Redox Potential

The Listowel marsh systems demonstrated peak dissolved oxygen levels in spring and fall and varying degrees of oxygen depletion in the summer and winter (Figure 2). The lowest levels occurred in summer when oxygen concentrations in the marsh effluents were generally at or near zero for one or more months. There was a progressive decline in oxygen in the marsh systems during the winter period of ice cover (usually lasting from December through March). The winter decline was often followed by oxygen peaks resulting from spring algal blooms.

The pattern of changes in sediment redox potential at a depth of 1.5-2 cm reflected the variations in dissolved oxygen in the wastewater. Most measurements were between -100 and +240 mV, the zone of facultative anaerobic respiration. A decline in redox potential close to or below -100 mV (the range in which true anaerobes, e.g. sulphate-reducing bacteria, predominate) was measured in summer whereas decreases in redox potential in winter were not as severe. Reductions in treatment efficiency (based on mass balances of wastewater constituents) were observed during the steep decline in redox potential (around -300 mV) in the summer of 1983 when the unusually high evapotranspiration rates caused the formation of stagnant pools of anoxic wastewater.

Both types of pre-treatment had shortcomings with respect to the maintenance of aerobic metabolism in the marshes. The lagoon effluent was usually anoxic in winter due to the ice cover barrier to oxygen transfer and, due to the deep placement of the outflow pump, was uncharacteristically low for lagoons in summer when extensive algae growth is common. The aeration cell did not have sufficient capacity to sustain adequate oxygen levels in the wastewater, particularly during the summer months, and the high solids levels increased the oxygen demand in the marsh. The growth of duckweed on the marsh water surface in summer and the ice cover in winter impeded diffusion of atmospheric oxygen into the marshes.

2. Suspended Solids

Monthly average suspended solids concentrations in the marsh system effluents were generally below 15 mg L^{-1} from fall through spring (Figure 3), often 5 mg L^{-1} or less for extended periods. Elevated concentrations of suspended solids occurred in one or more years in all systems in summer or late spring as a result of algae growth. This was compounded in summer by the concentration of suspended material resulting from evapotranspiration. The high suspended solids loadings from the complete-mix aeration cell effluent caused the development of sludge deposits at the influent end of System 4. These disrupted flow, caused die-back of the cattails and contributed to an elevated oxygen demand in the marsh, but did not significantly affect the marsh effluent levels of suspended solids which were comparable in both systems.

3. Five-Day Biological Oxygen Demand

Marsh effluent BOD-5 levels were generally less than 15 mg L^{-1} during the ice-free months, often between 5 and 10 mg L^{-1} (Figure 4). In the period of January through March, the monthly average BOD-5 levels in Systems 3 and 4 rose slightly in some years to maximum monthly average levels of 26 and 23 mg L^{-1} , respectively. Although low winter temperatures result in reduced microbial activity, substantial reductions in BOD-5 were achieved during the winter months. At

loadings experienced in the last three years of the study, winter removal efficiencies ranged between 58 and 82% in System 3 and between 92 and 98% in System 4. Increases in BOD-5 levels occurred occasionally in one or more summer months, reaching maximum monthly concentrations of 32 and 34 mg L⁻¹ in Systems 3 and 4, respectively. The elevated summer BOD-5 levels were in most cases coincident with increases in suspended solids concentrations.

4. Phosphorus

Marsh effluent levels of total phosphorus were generally below 1 mg L⁻¹ and often below 0.5 mg L⁻¹ in the period of fall through spring (Figure 5). Elevated total phosphorus levels occurred in summer (usually July) at which time 67-82% of the total phosphorus was in the soluble fraction. Monthly average total phosphorus values in System 3 exceeded 1 mg L⁻¹ during the summer of 1981 (May-Oct.) when alum treatment was suspended and in the summer of 1983 during a period of severe oxygen depletion. System 4 showed higher summer peak total phosphorus levels which occurred in all years and were sustained for more than one month. Marsh effluent soluble phosphorus levels were generally <0.4 mg L⁻¹ (often <0.2 mg L⁻¹ in spring and fall), increasing in summer to maximum monthly average levels of 1.2 mg L⁻¹ in System 3 and 2.2 mg L⁻¹ in System 4.

The decline in annual soluble phosphorus removal in Systems 3 and 4 with increases in the cumulative soluble phosphorus loadings is illustrated in Figure 6. Similar results have been reported in several different types of wetlands used for wastewater treatment (Richardson, 1985). The decline in soluble phosphorus removal efficiency over the four years indicates a reduction in the phosphorus adsorption capacity of the sediment and suggests phosphorus saturation of the sediment. Soluble phosphorus in marshes is reported to be immobilized by adsorption and precipitation reactions with aluminum, iron, calcium and clay minerals (Nichols, 1983). The mineral and clay content of the sediment in the Listowel marsh systems was relatively stable due to, the absence of stormwater drainage in the marsh influent and, therefore, the creation of few, if any, new inorganic adsorption sites. Factors contributing to the decline in phosphorus retention were the extended periods of oxygen depletion and the high organic and

phosphorus loadings in System 4. Reports indicate that a major mechanism of phosphorus retention in sediments is adsorption onto oxyhydroxides of iron and aluminum (Hook et al, 1973; Day, Jr and Kemp, 1985).

Although the data indicate an annual net export of soluble phosphorus by the end of the study, when summer marsh effluent oxygen levels remained above 2 mg L^{-1} (which occurred in System 3 in 1984 only), 84% soluble phosphorus removal was achieved and soluble phosphorus levels remained $\leq 0.07 \text{ mg L}^{-1}$ in all months. Total phosphorus levels in System 3 effluent during the same summer remained $\leq 0.2 \text{ mg L}^{-1}$. It may be possible, therefore, that with chemical phosphorus reduction and the maintenance of sufficient dissolved oxygen in the wastewater (to prevent mobilization from the sediment), effluent phosphorus levels can be sustained at low enough levels to meet discharge criteria over the long term.

5. Nitrogen

Marsh effluent total Kjeldahl nitrogen (TKN) concentrations were lowest in the spring and fall ($\leq 10 \text{ mg L}^{-1}$, often $\leq 5 \text{ mg L}^{-1}$). Increases occurred in winter ($\leq 15 \text{ mg L}^{-1}$ in System 3 and $\leq 17 \text{ mg L}^{-1}$ in System 4) and summer ($\leq 13 \text{ mg L}^{-1}$ in System 3 and $\leq 23 \text{ mg L}^{-1}$ in System 4). On average during the four years, ammonia comprised 63% and 70% of the TKN in the effluent of System 3 and 4, respectively, and showed a similar pattern of variation in the marsh effluents (Figure 7). Monthly effluent ammonia levels declined to $\leq 1.0 \text{ mg L}^{-1}$ for varying lengths of time in the spring and early summer in System 3, whereas ammonia levels in the effluent of System 4 decreased to $\leq 3.0 \text{ mg L}^{-1}$ during this period.

Elevated ammonia levels were observed in the summer and winter in all marsh systems. Ammonia treatment efficiencies were lowest in winter; the decline in ammonia removal began in December or January and lasted through March. Maximum monthly average concentrations were 13 mg L^{-1} and 16 mg L^{-1} in the effluent of Systems 3 and 4, respectively. System 4 showed little ammonia removal during influent peaks in summer and winter with effluent levels often exceeding influent levels. The data suggest that nitrification was inhibited in summer by an inadequate oxygen supply whereas in winter low water temperatures appear to have

been the major limiting factor, although low oxygen levels may have also contributed to reduced nitrification. Ammonia in treated effluents could pose a danger to aquatic life in a continuous release system if the receiver does not provide adequate dilution to reduce the oxygen demand imposed by elevated ammonia levels and to maintain un-ionized ammonia below toxic levels. The Ministry surface water objective for un-ionized ammonia is 0.02 mg L^{-1} . Based on maximum levels in the marsh effluents, dilutions of 10:1 would be required to meet this criterion in a receiver with an elevated pH (i.e. pH=8).

6. Hydrogen Sulphide

Hydrogen sulphide levels in the marsh increased at the end of the winter and in summer when oxygen and nitrates were unavailable to satisfy the requirements of heterotrophic bacterial metabolism. Marsh effluent hydrogen sulphide levels remained low ($<0.5 \text{ mg L}^{-1}$) through the winter and early spring or in some years (even though lagoon-treated influent contained elevated levels) or remained low until February or March at which times concentrations rose to a maximum of 6 mg L^{-1} in Systems 3 and 4. The elevated hydrogen sulphide levels in the lagoon effluent during the period of ice cover (maximum 12.1 mg L^{-1}) in almost all cases showed improvement after treatment in marsh System 3. Hydrogen sulphide production in summer was observed in all marsh systems in months when sampling was conducted. In Systems 3 and 4, monthly summer levels rose to a maximum of 7.1 mg L^{-1} and 14.5 mg L^{-1} , respectively, whereas the nonchannelized systems exceeded these levels. The dilutions required to consistently meet Ministry objectives of 0.002 mg L^{-1} un-ionized hydrogen sulphide for the protection of aquatic life in surface waters could rarely be met in any of the experimental marsh systems.

7. Phenols

Phenol concentrations in the marsh effluent ranged between (1 and $24 \text{ } \mu\text{g L}^{-1}$) and followed a pattern similar to that of hydrogen sulphide as both reflected fluctuations in the availability of dissolved oxygen. The marsh systems receiving lagoon effluent (which contained a maximum phenol content of $21.5 \text{ } \mu\text{g L}^{-1}$) reduced phenols to low levels ($1.5 \text{ } \mu\text{g L}^{-1}$) in the first winter when oxygen concentrations were high. In other years large phenol reductions were observed in System 3 until the

end of winter when levels rose (maximum $18.5 \mu\text{g L}^{-1}$) in response to the increasing oxygen deficits under the ice. Similar trends were observed in System 4 effluent (maximum $12.5 \mu\text{g L}^{-1}$) although influent levels were low. In summer, phenol levels in the marsh effluents often rose above influent levels (maximum $14.0 \mu\text{g L}^{-1}$ in System 3 and $23.5 \mu\text{g L}^{-1}$ in System 4). Based on monthly average levels of phenols in the effluent of Systems 3 and 4, dilutions in the range of 14:1 would be required to regularly meet Ministry surface water guidelines of $1 \mu\text{g L}^{-1}$, a level set to avoid tainting of edible fish flesh.

8. Fecal Bacteria and Pathogens

Fecal bacteria reductions were high during most of the year with marsh effluent fecal coliform (FC) levels less than or equal to those of Ministry design objectives for disinfected secondary effluent (200/100 ml). However, elevated monthly geometric mean levels (maximum 8,000/100 ml in System 3) occurred in summer and/or winter (Table 1). The detection of maximum levels of FC in the winter months may result from longer bacterial survival at low temperatures (Berg, 1971) and the possibility of short-circuiting due to density stratification and ice blockages. The increases in FC levels in the summer months may be explained in part by the concentrating effect of evapotranspiration. However, the increased numbers of fecal bacteria in summer and winter coincided with the decline in sediment redox potential, and it has been suggested that these conditions give a competitive advantage to the fecal indicator bacteria which are facultative anaerobes (Palmateer et al, 1985). FC levels in the effluent of Systems 3 and 4 were similar although the influent levels in System 3 were 0.1-2.0 % of the levels in the influent of System 4.

Fecal streptococcus (FS) levels showed similar reductions and seasonal trends but the maximum monthly level was higher (maximum 17,000/100 ml in System 3) and generally peaked in July or September. FS has been shown to survive longer than FC at high temperatures (Berg, 1971). Substantial reductions in levels of bacterial pathogens were observed in the marsh system effluents (Table 2). The pathogens were generally detected in the effluent at low levels except for increases in some winter months. Increases in pathogenic bacteria in the effluent were associated with elevated FC levels.

Conclusions

The marsh systems were capable of producing effluent of secondary to tertiary quality. Four year average annual concentrations of the major wastewater contaminants in the influent and effluent of the channelized marshes and average annual treatment efficiencies are listed in Table 3. Large BOD reductions were measured throughout the year despite the low temperature of the wastewater ($\leq 2^{\circ}\text{C}$) in the winter months. Removal efficiencies for soluble phosphorus and ammonia were appreciably lower in System 4 indicating the importance of pre-treatment method on marsh system performance.

The oxygen budget proved to be a major influence on the efficiency of wastewater removal in the marsh systems. Although operating procedures permitted the regulation of marsh hydrology in the attempt to achieve optimal contaminant removal, reductions in treatment efficiency occurred in summer and/or winter during periods of low dissolved oxygen. Elevated levels of ammonia, hydrogen sulphide, phenols and phosphorus in the marsh effluent were generally associated with anaerobic conditions in the marshes. However, low water temperatures were probably responsible for much of the reduction in ammonia removal during winter months when oxygen levels were maintained above 2 mg L^{-1} and should have been adequate to support nitrification.

The data from the experimental systems suggested a number of improvements on marsh design and operation which have been incorporated into a full-scale marshland sewage treatment facility at Port Perry, Ontario. The major modification is the installation at Port Perry of the recommended pre-treatment unit which feeds wastewater to the marshes with a combination of consistently high oxygen levels and low concentrations of suspended solids, hydrogen sulphide, phenols and fecal bacteria. The pre-treatment unit is a 3.1-3.7 m deep partial-mix facultative aeration cell, with an average detention time of 30 days (to provide sludge storage capacity for 20 years) and chemical phosphorus reduction to about 1.0 mg L^{-1} total phosphorus.

The application of marshland wastewater treatment in Ontario depends on contaminant removal at a level which will produce an effluent quality suitable for year-round continuous discharge. A high effluent quality is particularly important in summer during periods of reduced flow and correspondingly low assimilative capacity in receiving waters. Although the problem of reducing ammonia concentrations to tertiary treatment levels ($<3 \text{ mg L}^{-1}$) may be more intractable in winter, limitations on marsh application will arise primarily from the sensitivity of receivers during the summer months. The effluent quality produced at Port Perry will provide a better indication of the potential for the application of this type of marshland sewage treatment in Ontario.

References

- Berg, G. 1971. Viruses and water quality occurrence and control. Proc. of the 13th Water Quality Conference, Univ. of Illinois, Urbana, Ill.
- Black, S.A. 1983. The use of marshlands in wastewater treatment. Proc. Technology Transfer Conference No. 4, Ministry of Environment, Toronto, Ontario, pp. 168-183.
- Brinson, M.M. 1985. Management potential for nutrient removal in forested wetlands. In: Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Godfrey, P.J., E.R. Kaynor, S. Pelczarski and J. Benforado (eds.) Van Nostrand Reinhold Co., N.Y., pp.405-414.
- Day, Jr., J.W. and G.P. Kemp. 1985. Long-term impacts of agricultural runoff in a Louisiana swamp forest. In: Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Godfrey, P.J., E.R. Kaynor, S. Pelczarski and J. Benforado (eds.) Van Nostrand Reinhold Co., N.Y., pp.317-326.
- Herskowitz, J. 1986. Listowel Artificial Marsh Project Report. Ontario Ministry of Environment. Water Resources Branch. 253 pp.
- Hook, J.E., L.T. Kardos and W.E. Sopper. 1973. Effects of land disposal of wastewaters on soil phosphorus relations. In: Recycling Treated Municipal Wastewater and Sludge Through Forest and Cropland. Sopper, W.E. and L.T. Kardos (eds.), Penn. State Univ. Press, University Park, pp.200-219.
- Nichols, D.S. 1983. Capacity of natural wetlands to remove nutrients from wastewater. JWPCF 55(5):495-505.

Ontario Ministry of Environment. 1981. Outlines of Analytical Methods. Laboratory Services Branch. 246 pp.

Ontario Ministry of Environment. 1984. Water Management: Goals, Policies, Objectives and Implementation Procedures of the Ministry of Environment. Water Resources Branch. 70 pp.

Palmateer, G., W.L. Kutas, M.J. Walsh and J.E. Koellner. 1985. Recovery of pathogenic and indicator bacteria from wastewater following artificial wetland treatment of domestic sewage in Ontario. In: Abstracts of the Ann. Meeting of the American Society for Microbiology, Las Vegas, 1985.

Reed, S., R. Bastian, S. Black and R. Kettry. 1985. Wetlands for wastewater treatment in cold climates. In: Future of Water Reuse, Proc. of Water Reuse Symp.III, vol.2, Aug. 26-31, 1984, San Diego, AWWA Research Foundation, Denver, pp.962-972.

Richardson, C.J. 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228: 1424-1427.

Wile, I., G. Miller and S. Black. 1985. Design and use of artificial wetlands. In: Ecological Considerations in Wetlands Treatment of Municipal Wastewaters. Godfrey, P.J., E.R. Kaynor, S. Pelczarski and J. Benforado (eds.) Van Nostrand Reinhold Co., N.Y., pp.26-37.

Wile, I., G. Palmateer and G. Miller. 1981. Use of artificial wetlands for wastewater treatment. In: Proc. of the Midwest Conference on Wetland Values and Management. Richardson, B. (ed.), June 1981, St. Paul, Minn., pp.255-271.

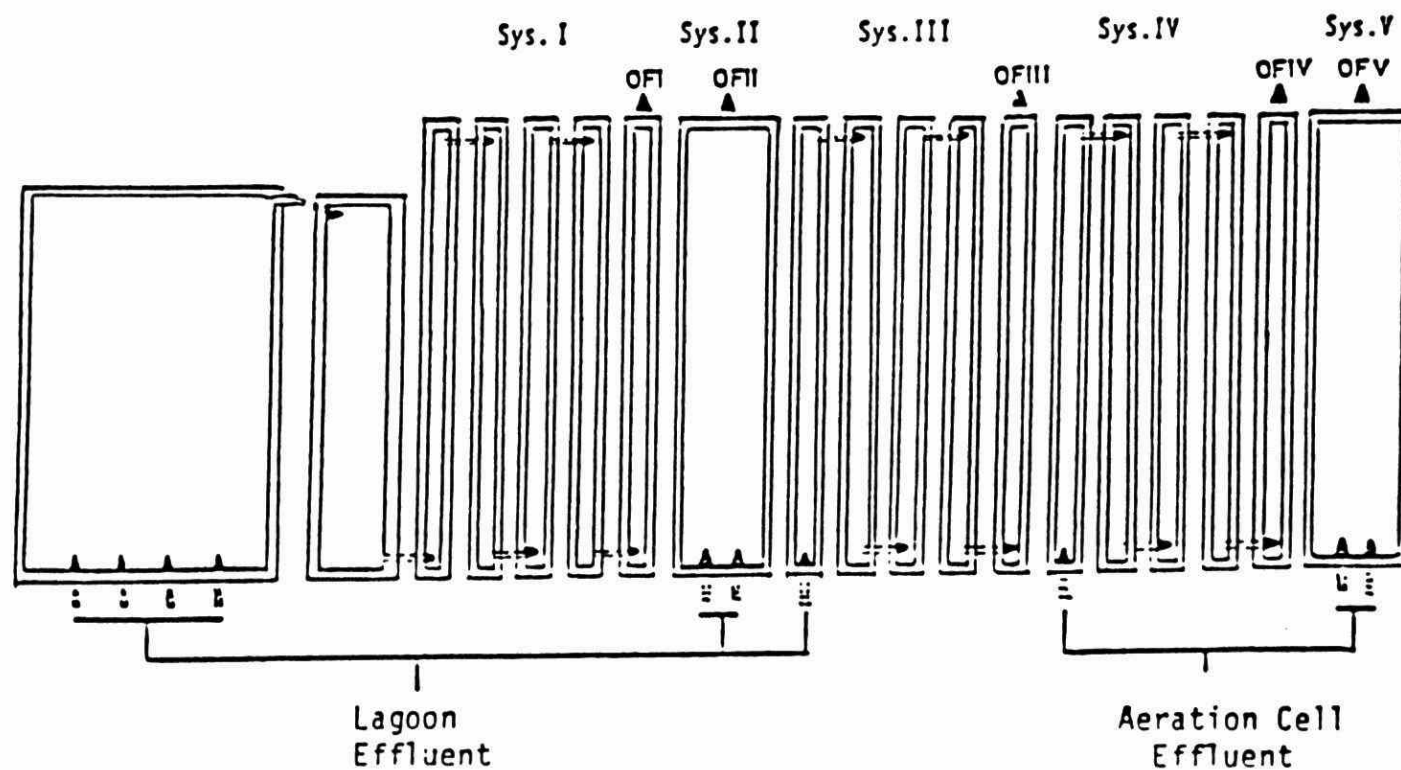


Figure 1. Design of Listowel marsh systems.

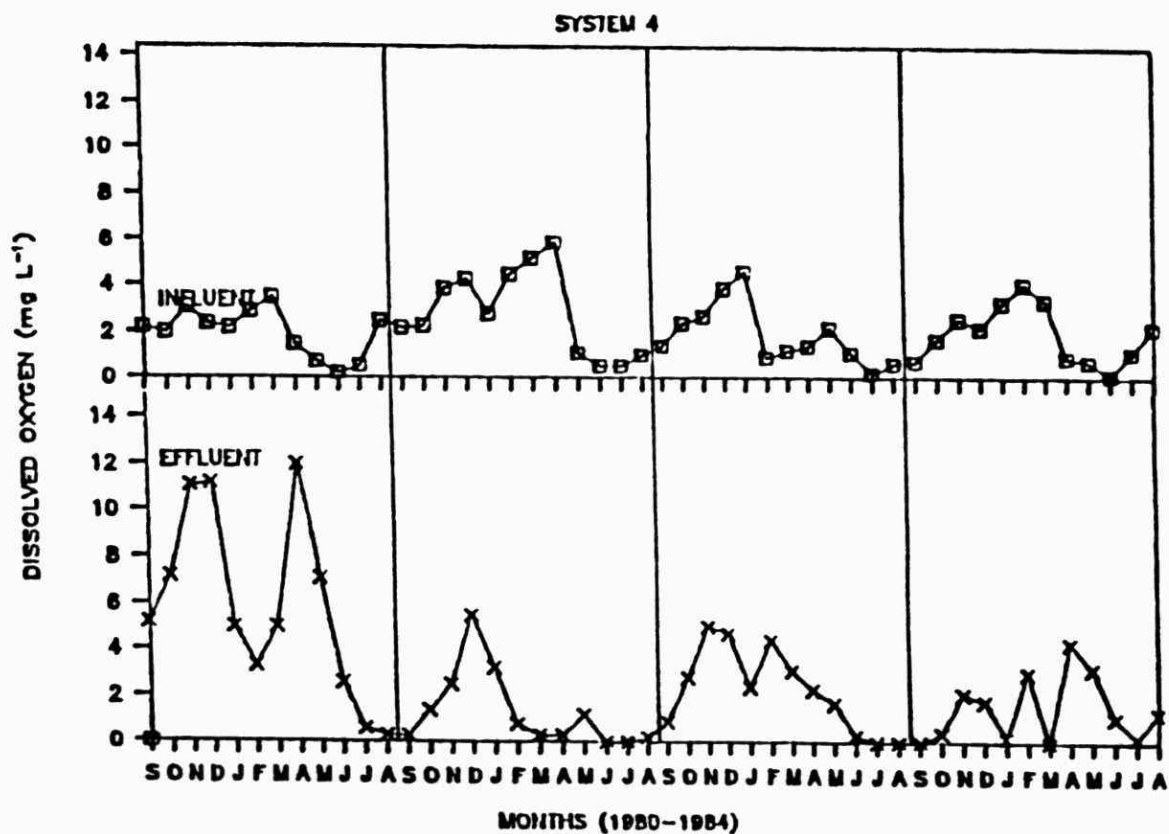
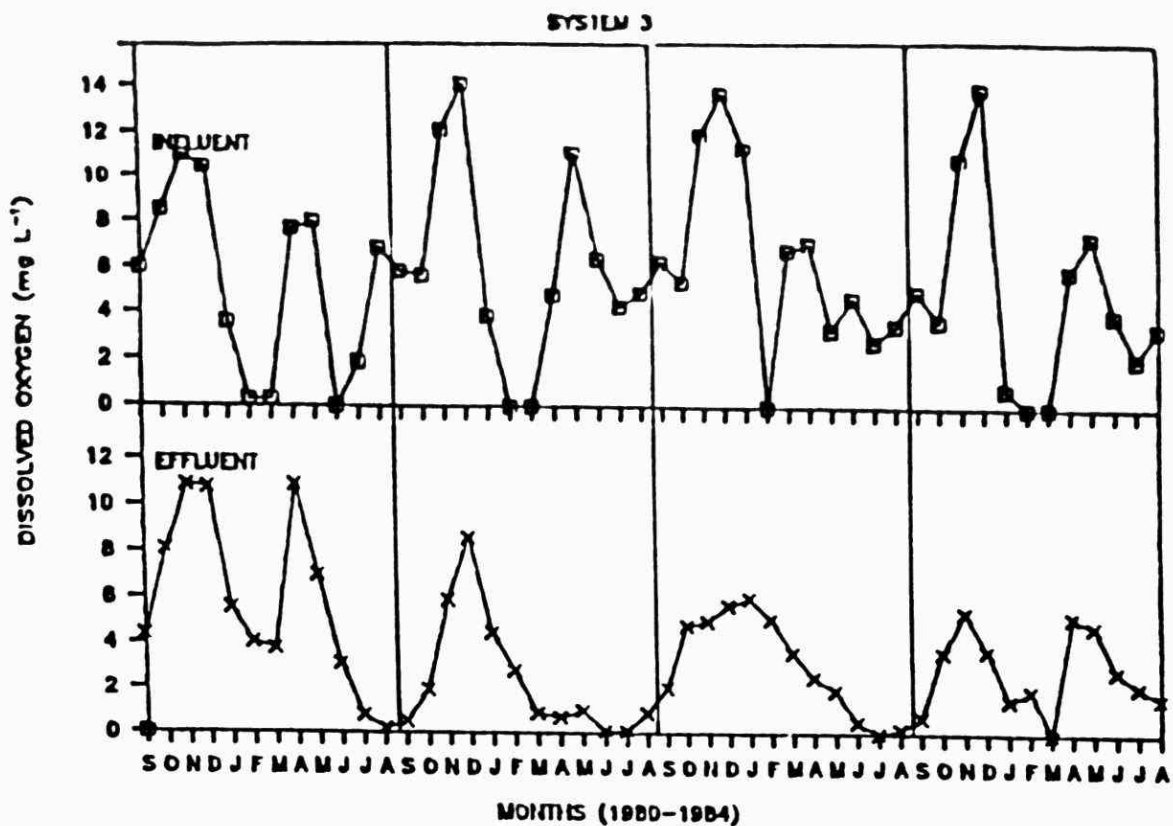


Figure 2. Monthly average dissolved oxygen levels in System 3 (treating lagoon effluent) and System 4 (treating aeration cell effluent).

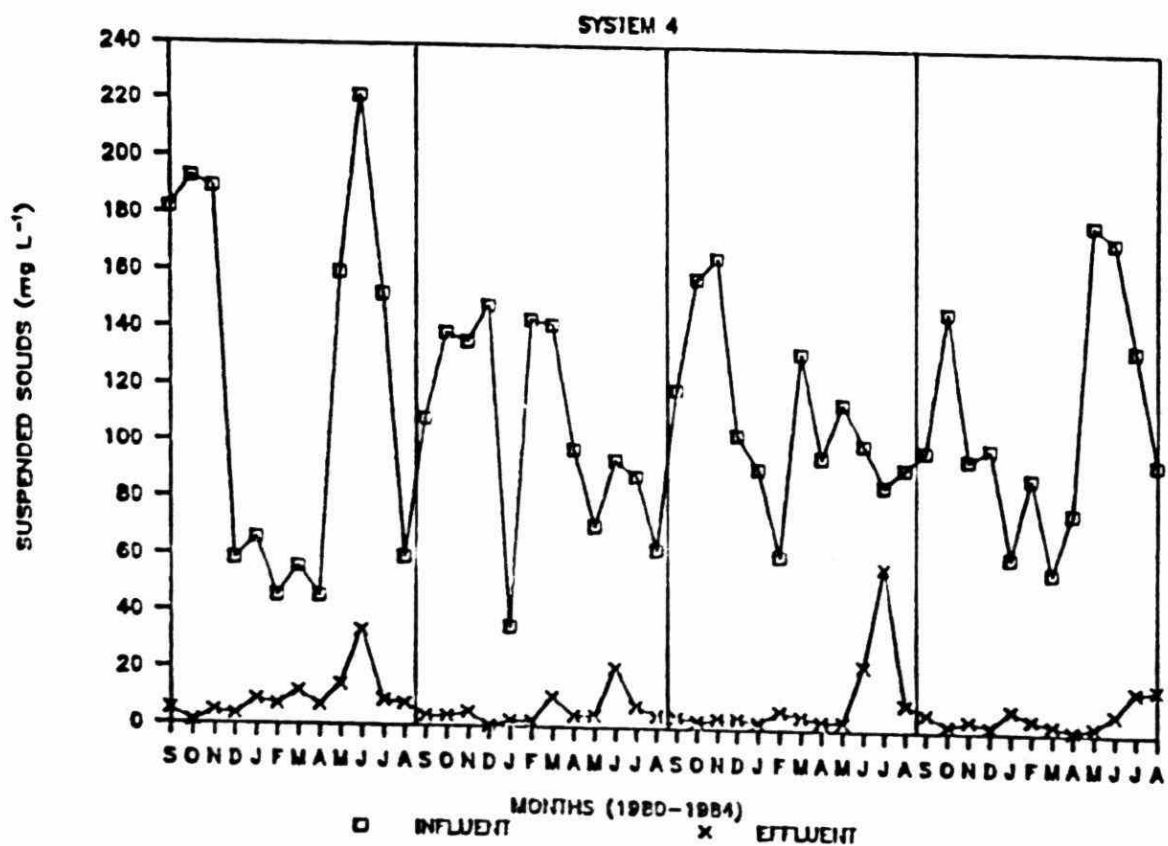
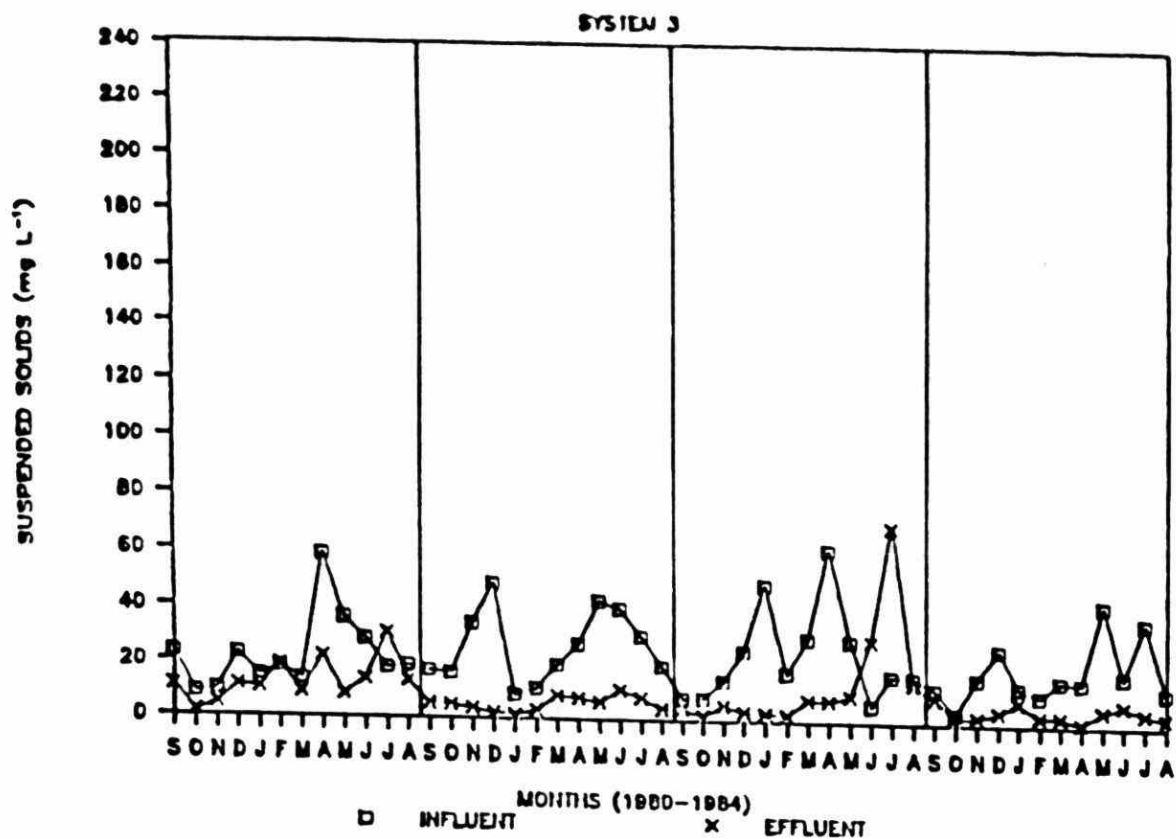


Figure 3. Monthly average suspended solids levels in the influent and effluent of Systems 3 and 4.

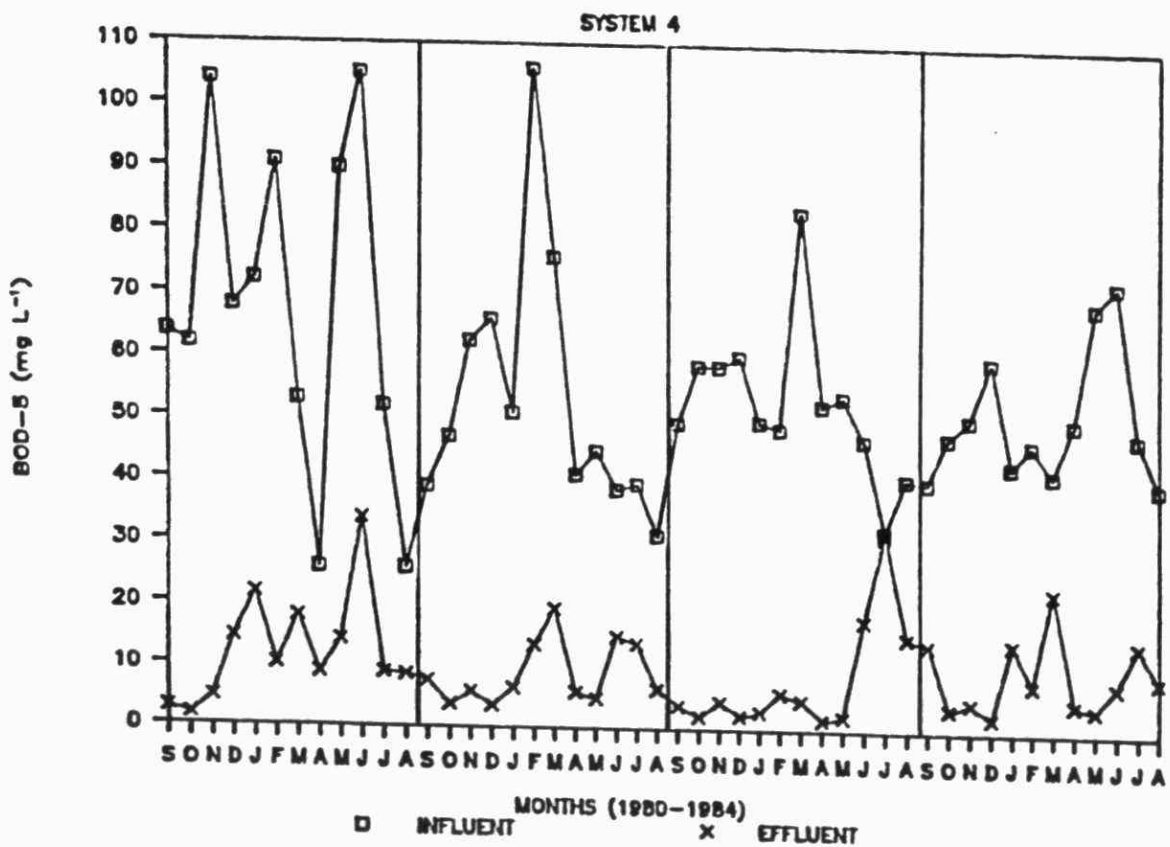
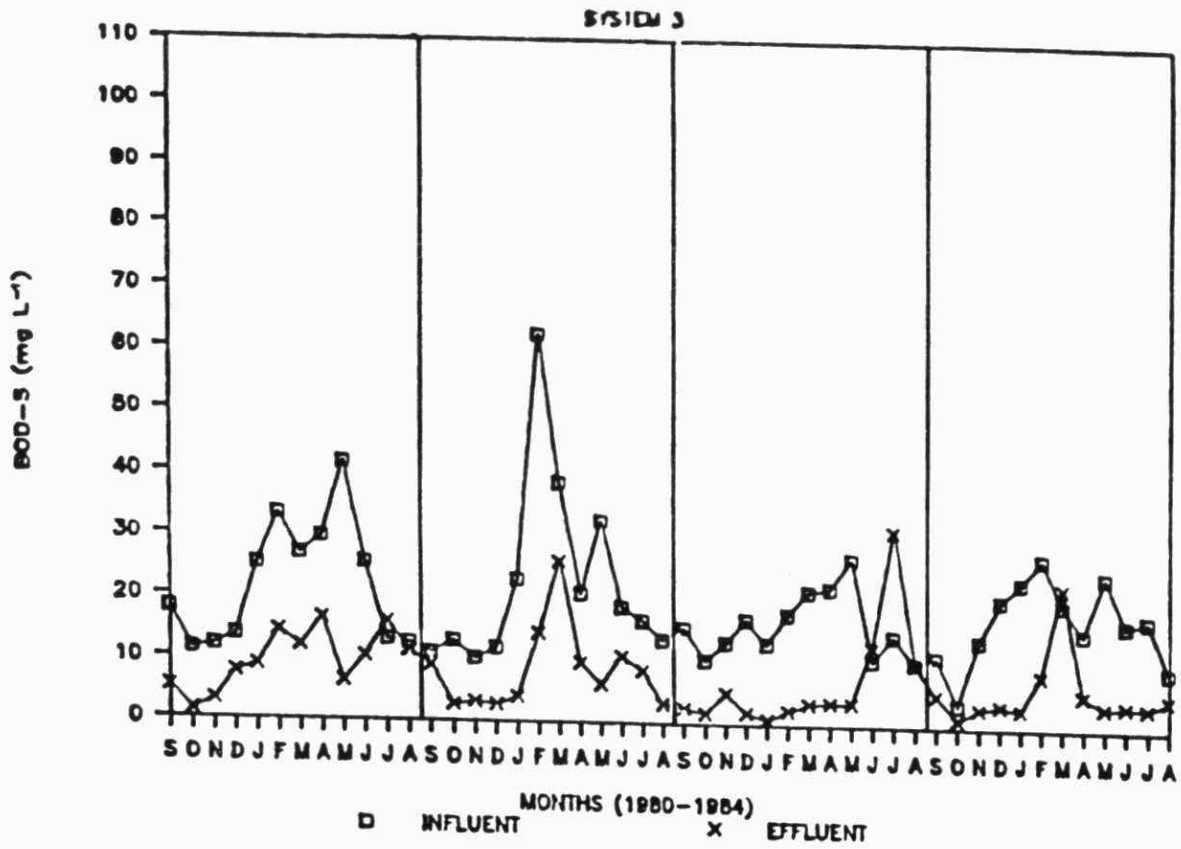


Figure 4. Monthly average BOD-5 levels in the influent and effluent of Systems 3 and 4.

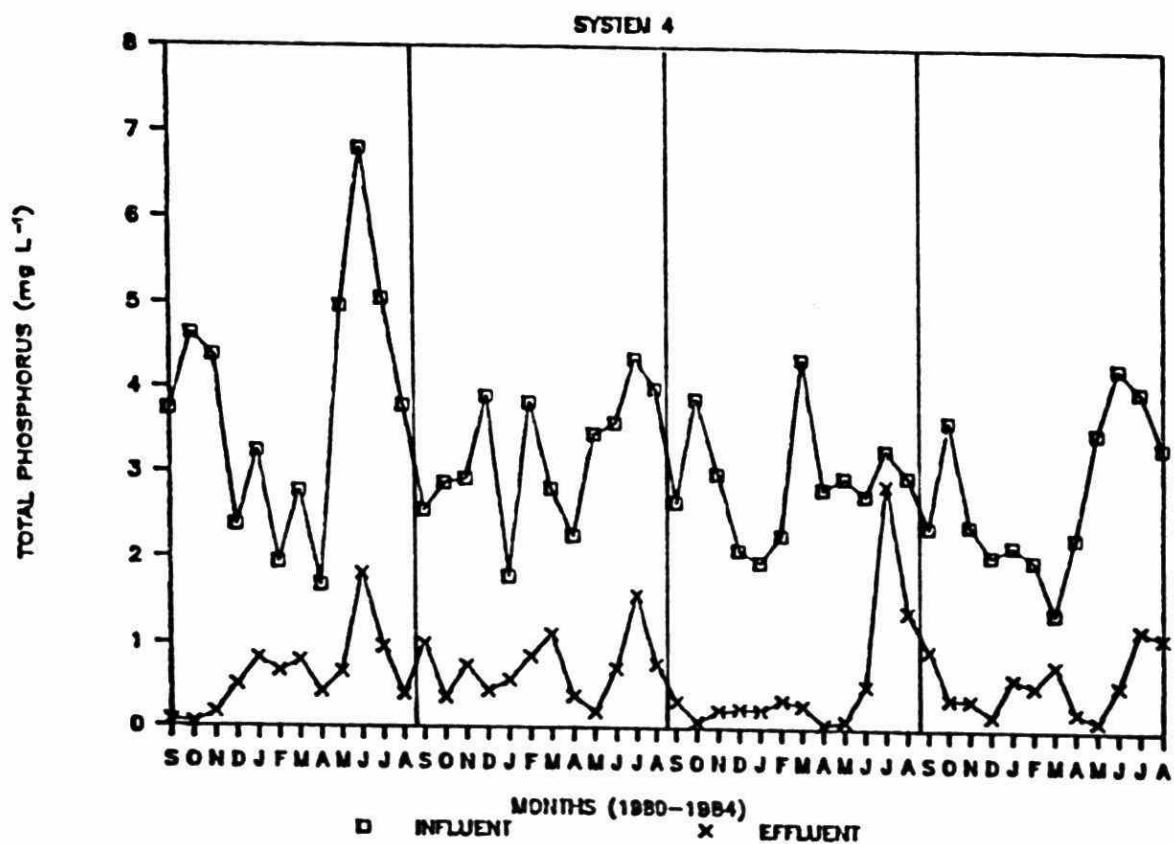
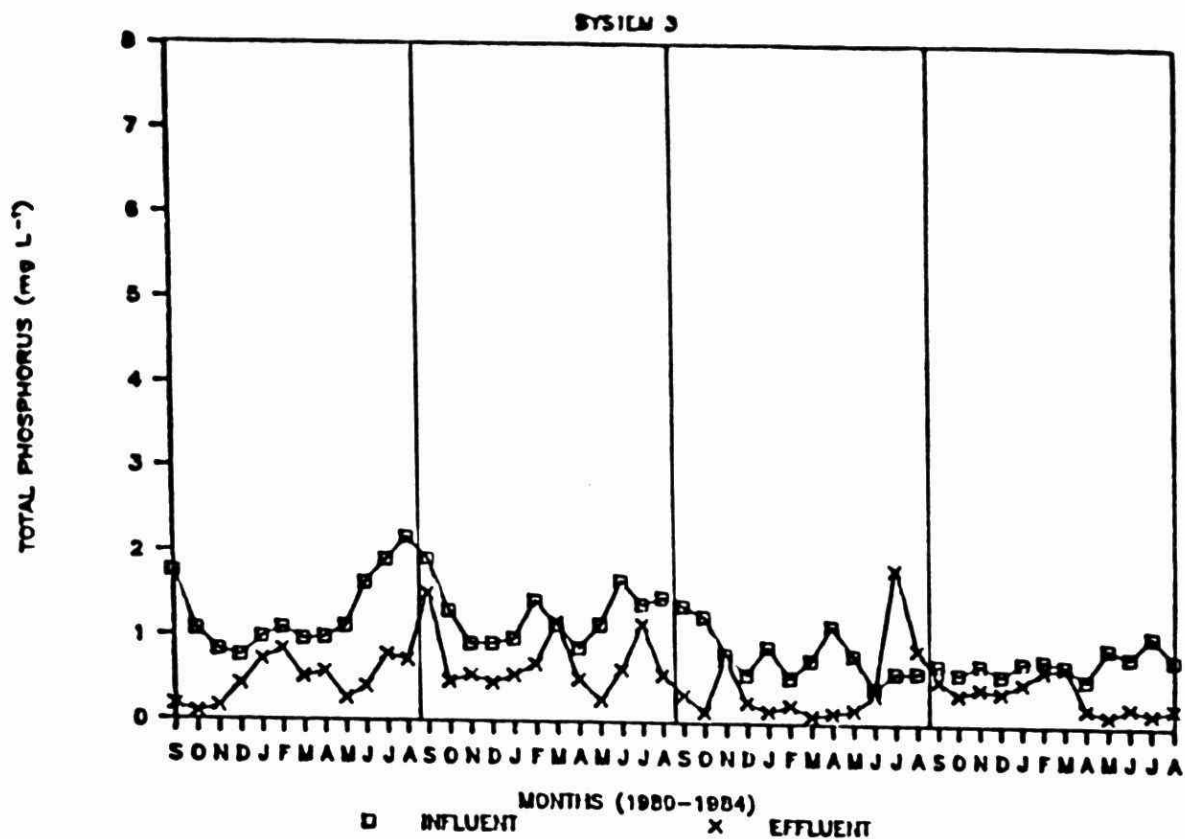


Figure 5. Monthly average total phosphorus levels in the influent and effluent of Systems 3 and 4.

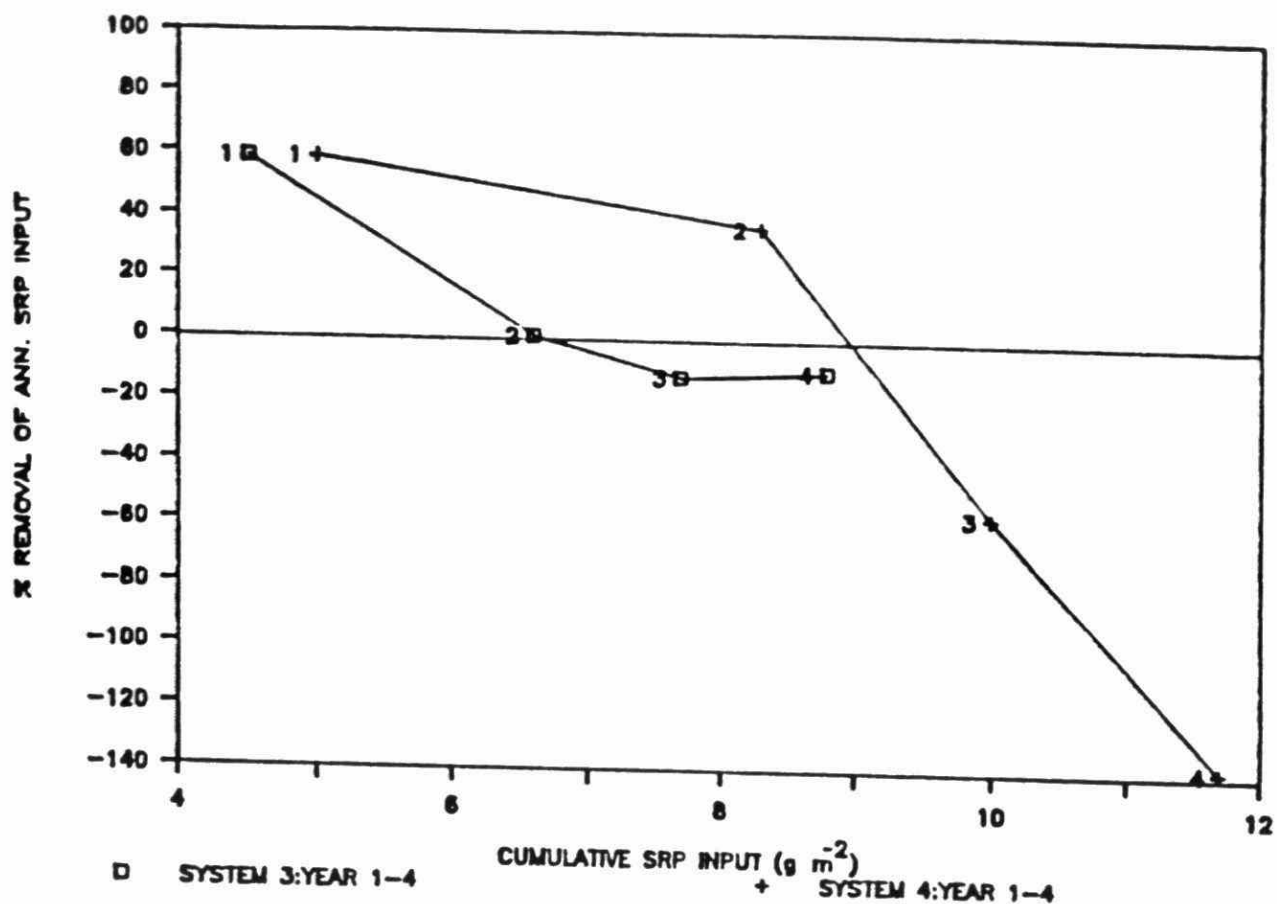


Figure 6. Cumulative soluble reactive phosphorus (SRP) loadings and annual removal rates in Systems 3 and 4.

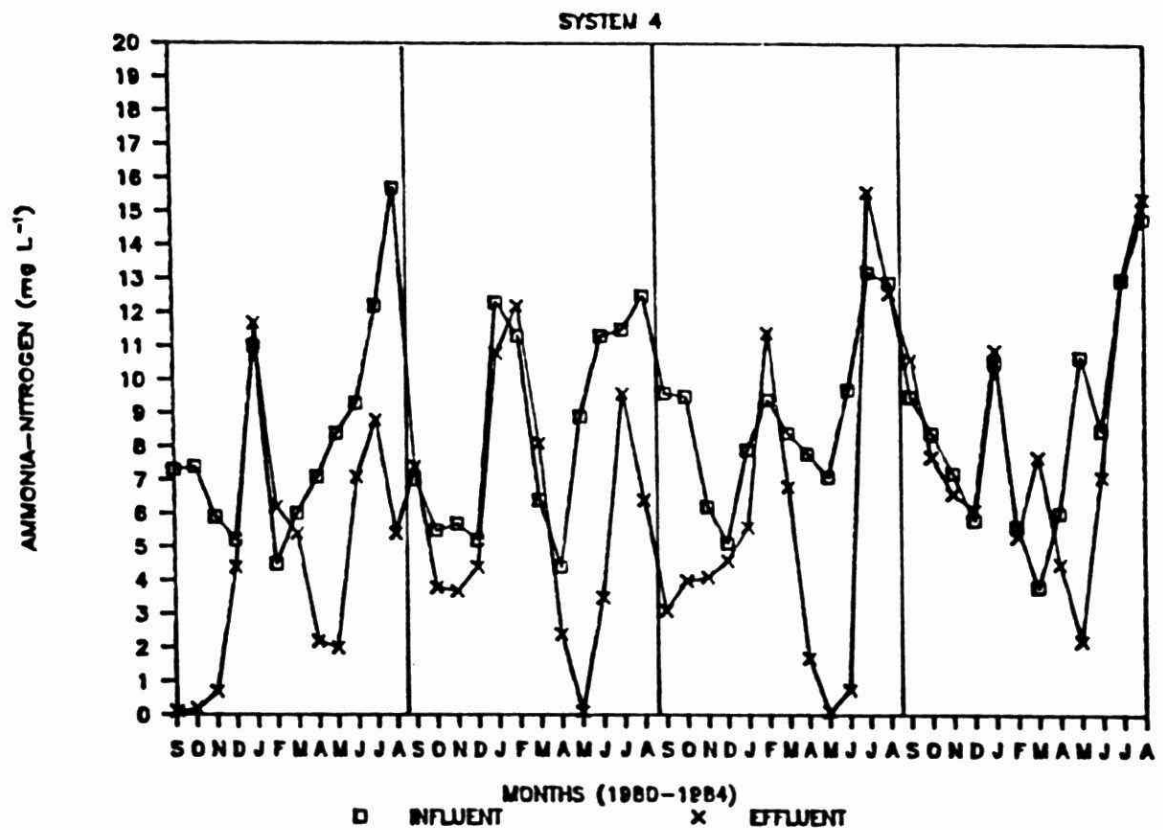
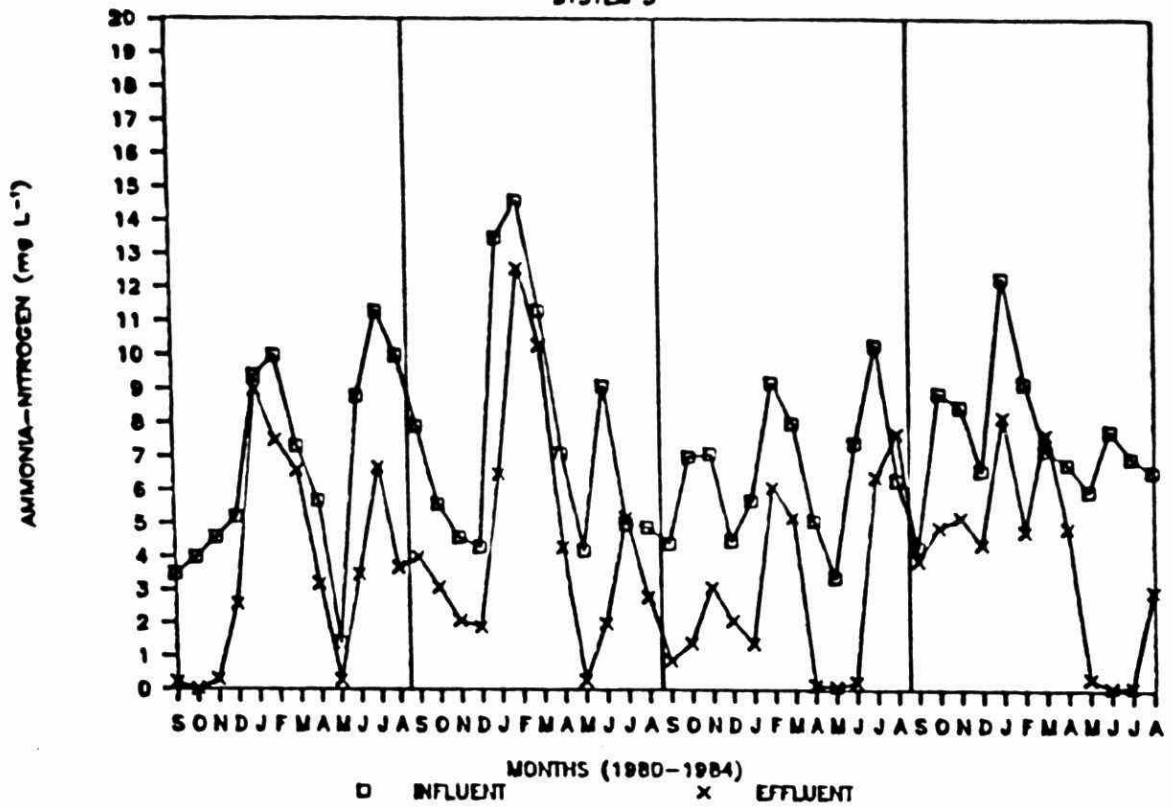


Figure 7. Monthly average ammonia-nitrogen levels in the influent and effluent of Systems 3 and 4.

Table 1. Monthly Average Geometric Mean Levels of Fecal Coliform Bacteria Over Three Years (1981-1984)

Month	System 3			System 4		
	Influent	Effluent	% Reduction	Influent	Effluent	% Reduction
Sept.	205	44	79	216,125	467	> 99
Oct.	573	21	96	314,647	248	> 99
Nov.	4,343	18	> 99	293,662	373	> 99
Dec.	3,095	36	99	421,269	57	> 99
Jan.	46,154	15	> 99	386,224	603	> 99
Feb.	80,678	223	> 99	382,320	1,017	> 99
Mar.	36,726	3,058	92	164,204	2,043	99
Apr.	3,544	109	97	169,275	34	> 99
May	626	37	94	172,472	27	> 99
June	288	641	-123	183,873	334	> 99
July	376	697	-85	182,240	1,353	99
Aug.	206	304	-48	153,736	297	> 99

Bacterial levels in numbers per 100 ml.

Table 2. Geometric Mean Levels of Fecal Coliform Bacteria (FC), Yersinia enterocolitica (YE), Clostridium perfringens (CP), Pseudomonas aeruginosa (PA) and Salmonella spp. (SSP) in the Channelized Marshes Over Three Years (1981-84).

	FC		YE		CP		PA		SSP	
	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
System 3										
Geometric Mean	1,736	53	4,241	300	1,036	6	10	1	-	-
Frequency of Occurrence	100%	100%	63%	63%	88%	48%	100%	100%	67%	8%
System 4										
Geometric Mean	222,990	121	28,602	563	13,148	4	662	2	-	-
Frequency of Occurrence	100%	100%	69%	75%	96%	39%	100%	100%	83%	25%

Influent (Inf) and effluent (Eff) bacterial levels are in numbers per 100 ml. FC and PA tests conducted weekly (bi-weekly in winter); YE and CP tested predominantly in winter. SSP analyzed for presence or absence; samples (N=12) tested in alternate months in 1981 and 1982.

Table 3. Average Wastewater Concentrations and Treatment Efficiencies in Systems 3 and 4 (1980-1984)

System 3: Channelized marsh receiving lagoon effluent

Parameters	Average Conc. (mg L ⁻¹)		% Removal Based on Mass Balance				
	Influent	Effluent	1	2	3	4	Avg.
Suspended Solids	22.8	9.2	40	75	53	73	61
BOD-5	19.6	7.6	57	56	63	62	59
Total Phosphorus	1.0	0.5	53	39	47	45	46
Soluble Phosphorus	0.37	0.26	59	1	-12	-10	9
Total Kjeldahl-N	12.0	6.1	32	41	54	46	43
Ammonia-N	7.2	3.8	31	32	51	42	39
Un-ionized Ammonia-N	0.13	0.01					
Nitrate-Nitrite-N	0.25	0.23					
Hydrogen Sulphide*	1.8	1.0					
Un-ionized H ₂ S*	1.31	0.65					

System 4: Channelized marsh receiving aeration cell effluent

Parameters	Average Conc. (mg L ⁻¹)		% Removal Based on Mass Balance				
	Influent	Effluent	1	2	3	4	Avg.
Suspended Solids	111.1	8.0	90	93	93	94	93
BOD-5	56.3	9.6	78	80	88	81	82
Total Phosphorus	3.2	0.6	79	76	84	78	79
Soluble Phosphorus	0.40	0.34	59	37	-57	-138	-25
Total Kjeldahl-N	18.7	8.7	49	46	55	41	48
Ammonia-N	8.6	6.1	28	22	35	5	23
Un-ionized Ammonia-N	0.07	0.02					
Nitrate-Nitrite-N	0.38	0.21					
Hydrogen Sulphide*	0.20	1.31					
Un-ionized H ₂ S*	0.13	0.81					

* The dates and frequency of hydrogen sulphide analyses varied between years; most samples collected in winter.

Tests of a Hydrocyclone Designed for Sewage Treatment

by J.D. Boadway

Report on Project No. 184 PL

Summary

This report deals with pilot plant tests of a hydrocyclone designed for use in sewage treatment.

The unit proved capable of handling 36.4 liters/second of inflow when a differential pressure of 6 meters of water was applied. The reject flow could be varied from 0.5 to 5.0 liters per second by use of differing sizes of reject orifice and differing outlet pressures.

The unit achieved 100% removal of the grit used in tests which included sand particles of 60 microns in diameter and also removed fine sawdust and organic material from vegetable washings.

This hydrocyclone can be operated at low pressures and was designed specifically for use in sewage treatment. This may prove to be a new and useful tool and is now ready for field trials. The decision as to the nature and location of those trials needs now to be decided by the Ministry.

Introduction

The Ministry of Environment informed the author in June of 1985 of a grant, known as Project No. 184 PL, to develop a special design of hydrocyclone, which could be used with low pressure differential, to remove grit from sewage. The original proposal was that a unit would be designed after consultation with the Ministry. This design would then be built and tested at Queen's University. Finally any necessary modifications would be made to the unit and it would be installed in a sewage treatment plant for field testing.

A report (Ref. 1) was written by the author and submitted to the Ministry on August 6, 1985. This report discussed the theory of hydrocyclone design and outlined the design parameters of a hydrocyclone with their probable effects. Following a discussion with Mr. Henry Kronis, the liaison officer with the Ministry, a hydrocyclone deemed most suitable for sewage treatment was designed and a report (Ref. 2) sent to the Ministry to describe the final design and its expected performance. Blueprints of the unit were sent out for quotes from three possible fabricators. The installation for testing the equipment was designed while waiting for their response as reported in the author's spring report (Ref. 3).

The lowest construction bid was from Wejay Machine Products Company of Kingston. However, because the design was much larger in size than that anticipated when submitting the original proposal it was necessary to reduce the scope of the project slightly by having only one of the alternate cone designs built and to use for construction of the hydrocyclone funds which had

originally been intended for other aspects of the research. The unit was delivered in late April and work begun upon the test installation. Whereas the completion of the installation was expected by the first of July, diversion of personnel to other work and problems in erecting the equipment delayed completion until the second week in August. Students were employed as research assistants until September 12 and tests conducted to give the results presented in the report that follows.

While employed in the paper industry between 1952 and 1963, the author was involved in research on hydrocyclones, which were marketed under the tradename of "Vorject" and "Vorvac," and has also been studying the present design of hydrocyclone since 1978, and has taught environmental engineering for 20 years. The report will hence include remarks which stem from experience and unpublished information as well as the observations from the brief period of test on the unit and published papers of other investigators. Attempts will be made to avoid excessive repetition of material covered in the previous reports to the ministry.

Hydrocyclones

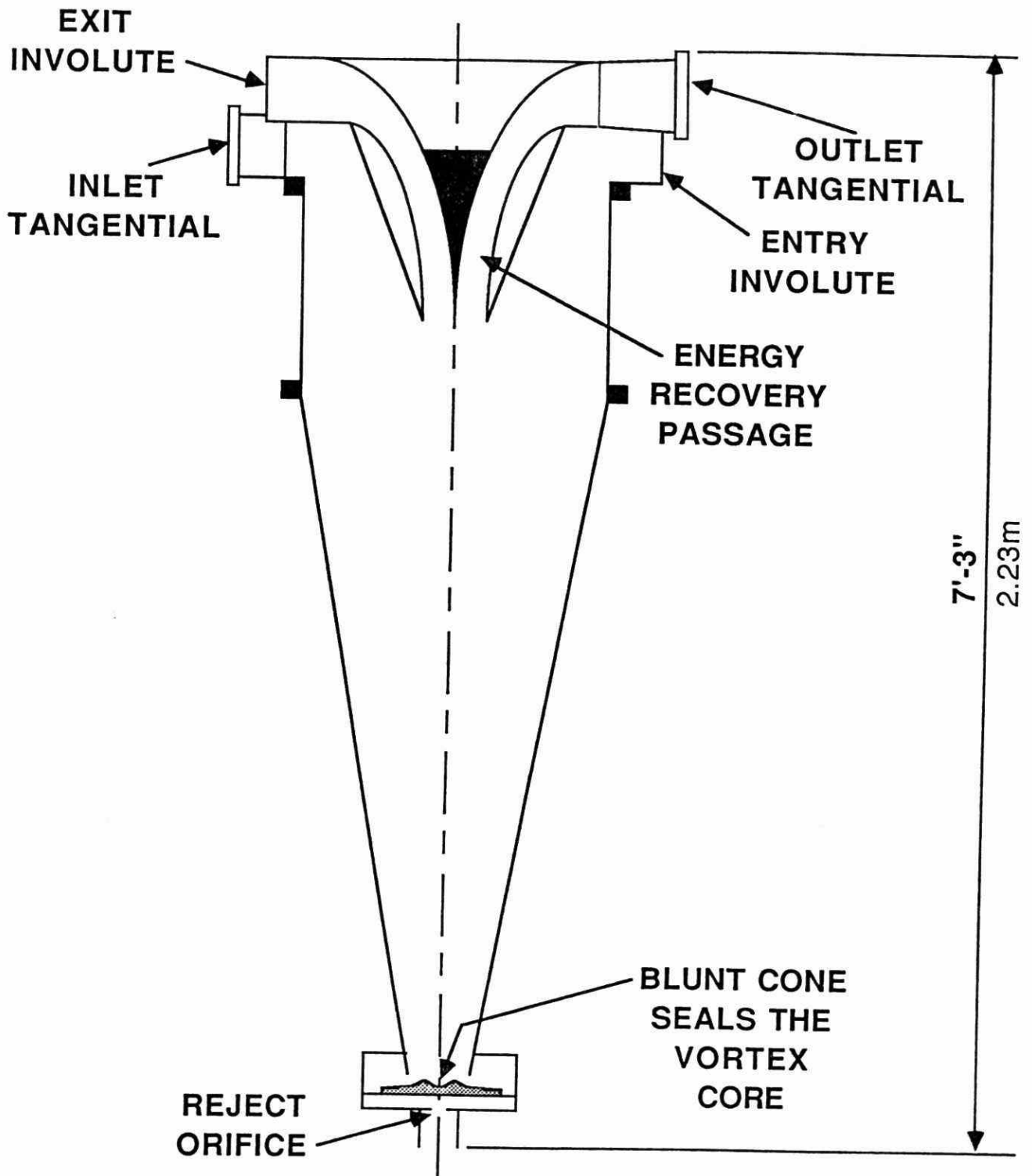
Hydrocyclones could be loosely defined as fluid containers in which a vortex is produced with sufficient resulting centrifugal force to bring about a separation. The text written by Bradley (Ref. 4) defines the broad range of these devices used for different purposes and dwells, for a considerable length, on the more common conical type. The early device of Freeman, sold under the name "Vortrap", was used for some time in sewage treatment (Ref.5). This device, which operated at low pressure drop, was developed in the paper industry for removal of grit and tramp metal.

There also has been use of the conical design known as the "Dorclone" (Ref. 6) for washing of grit. There have been attempts to use existing commercial designs of fluid cyclones but blockages have usually led to operating problems.

In more recent times there has been some use of a device called a "Swirl Chamber" (Ref. 7) in sewage treatment. This device is not a hydrocyclone but merely a circular clarifier of very high overflow rate in which the secondary currents induced in the boundary layer are used in place of mechanical arms to convey the settled solids.

To the author's knowledge there has not been any attempt to design a hydrocyclone specifically for use in sewage treatment. Such a design should operate at lower pressure, be very flexible in operating pressures to accommodate changes in flow and should, if possible, be free from problems of blockage from foreign objects so that it can operate without protection from screens. It should be capable of removal of all mesh sizes of grit and courser organic sediments. The development of a form of hydrocyclone, in which the energy in the exit fluid is converted into pressure, showed excellent promise of meeting that need and led to the submission of the

Figure 1 Energy Recovery Hydrocyclone



proposal to the Ministry and the grant of Project No. 184 PL.

The design which resulted was described in Reference 2 and the final version as manufactured for tests is shown in Figure 1. Fluid enters by an involute inlet, to minimize energy loss by turbulence, into a cylindrical section forming a vortex. The high tangential velocity, which becomes even larger as the fluid spirals inwards to smaller radii, leads to centrifugal forces which cause dense solids to migrate outward to the boundary layer next the wall. This boundary layer carrying the particles moves downward along the wall of the cone, due to the radial pressure gradient, and passes outward around a blunt cone and then spirals inward to discharge through a bottom orifice.

What makes this design special is that the fluid leaving the top passes through a gradually expanding coaxial passage which curves outward to an involute exit. This converts velocity in the vortex to pressure and results in a sucking effect which creates a vacuum at the core of the vortex. The conical barrier at the bottom end prevents air insuction and provides a recess for stabilizing the bottom end of the vacuum core. A net result is that whereas the pressure at the core of most hydrocyclones is atmospheric pressure, there is a vacuum at the core of this design. The larger pressure differential across the vortex leads to a high flow and tangential velocity especially when the inlet pressure and differential pressure are low. Thus the hydrocyclone can operate and separate effectively at lower pressures. In addition, since the reject end has a baffle which prevents air insuction, the unit can operate with both outlet and inlet pressures varied over a broad range.

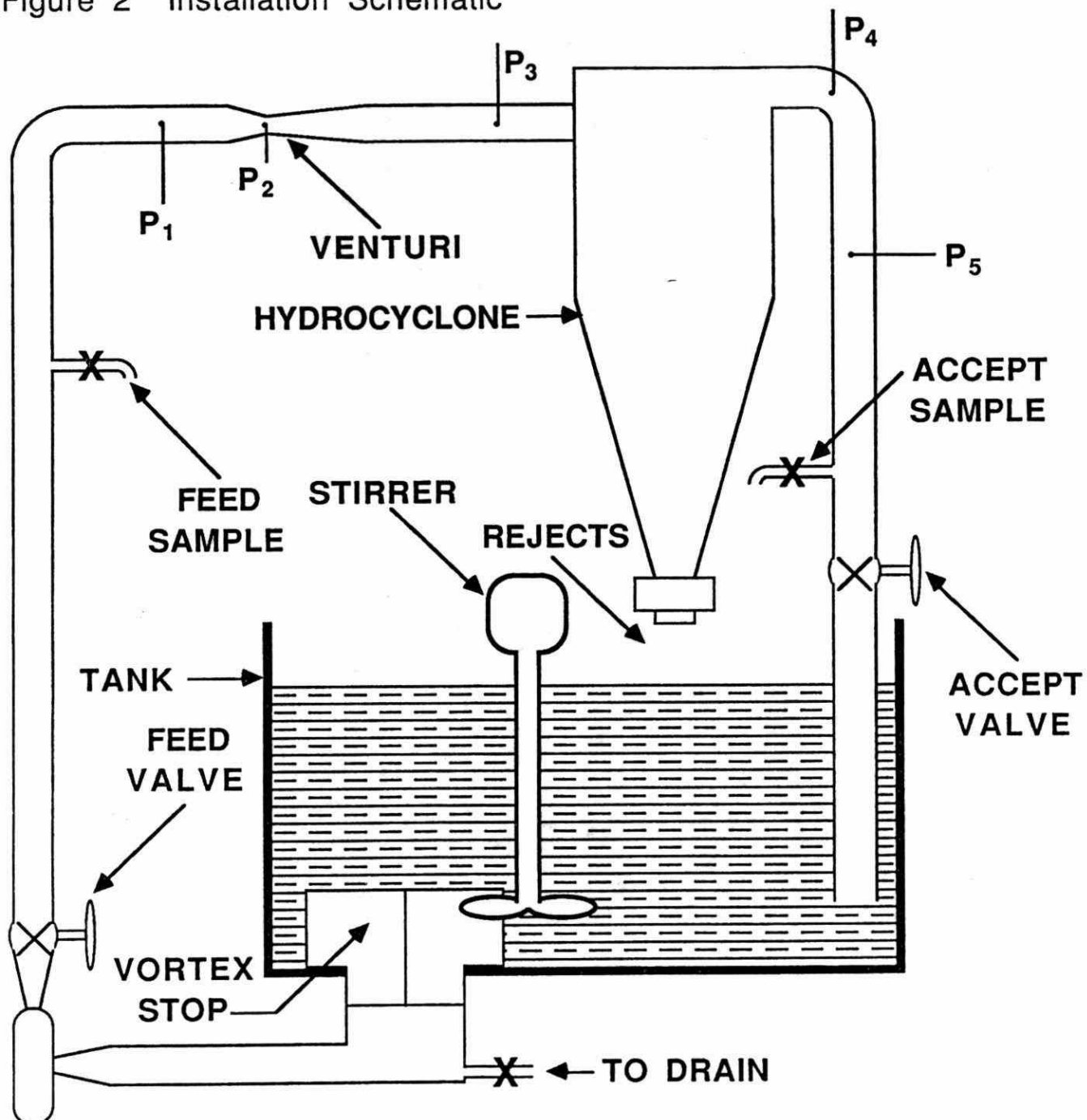
The unit shown in Figure 1 is the straight cone version indicated as an alternate in the previous design report. It was decided not to build the more expensive curved cone design because of limited funds available. The curved cone is thought to give better separation in oversize solids, less abrasion and a lower reject flow. Also, whereas the original design showed the curved exit surfaces as being made of fibreglass, the fabricator chose to make some parts of expanded aluminum. The unit cost \$10,600 of which a portion was for tooling.

Test Installation

The pilot plant installation is shown schematically in Figure 2 and also in the photograph Figure 3.

The tank had been used for previous tests on smaller hydrocyclones but had to be modified to accommodate the larger outflow without leading to a vortex at the outlet. The pump was well under capacity for handling the larger flow and thus limited the pressure which could be applied. The high velocity through the pump may have contributed to turbulence in the inlet fluid and pressure fluctuations.

Figure 2 Installation Schematic



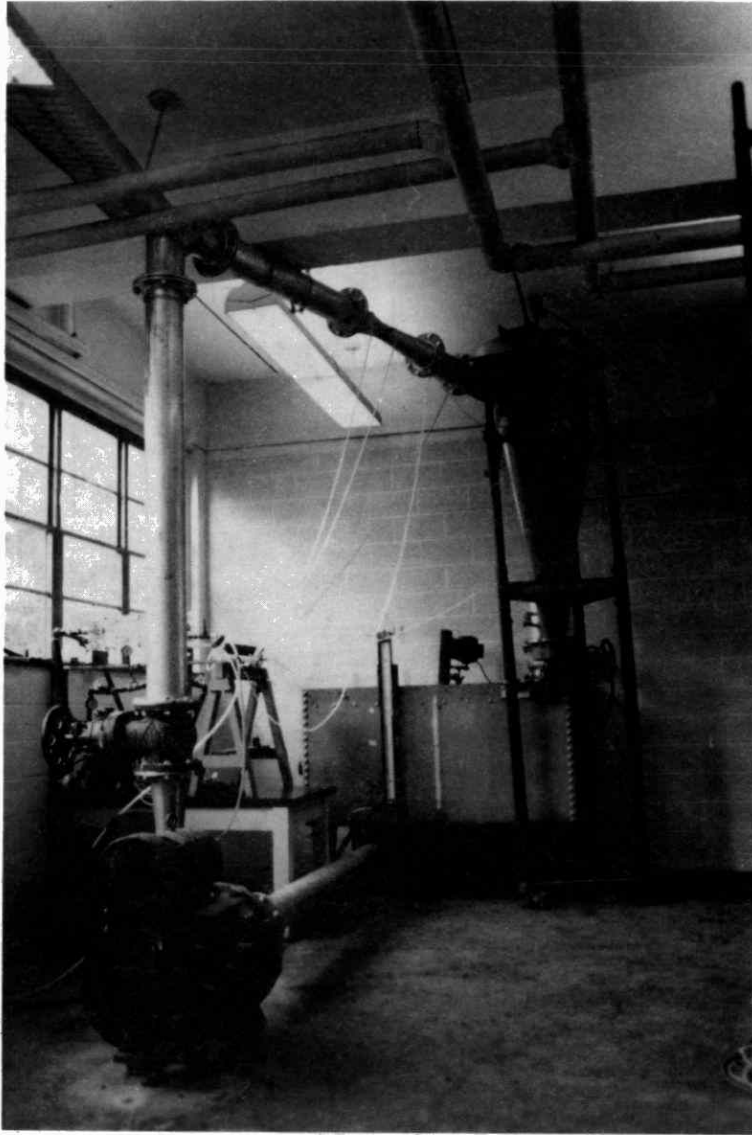


Figure 3 Test Installation

The piping system was of 6" aluminum tubing with standard 25 lb flanges. Gentle tapered reducers were fabricated to connect to the 4 inch inlet and 3 inch outlet of the pump. A Venturi meter was constructed for measuring the inlet flow and calibrated in Queen's hydraulics laboratory. The hydrocyclone was supported by a metal frame and also by a cable connected to an eye bolt through the floor into the office above.

Pressure measurements were taken at 5 locations, namely:

1. Inlet to the Venturi meter
2. Throat of the Venturi meter
3. Inlet to the hydrocyclone
4. On the side of the elbow on the exit
5. On the down pipe for the hydrocyclone

While a sensitive digital pressure meter had been purchased for the project, it was found to be unsuitable due to pressure fluctuations and a mercury manometer was used to measure the pressures during tests.

Hydraulic Tests

1. Scaling

It is essential to have detailed knowledge of the hydrocyclone to design future installations. It is also desirable for the author to have detailed hydraulic knowledge to ensure that the unit is performing according to design and to provide him with the background to design other units.

The unit being tested has a diameter of 25 inches (63.5 cm) and length of 7.4 feet (2.32 meters). It has been scaled up by a factor of 2.5 from a unit which had been tested previously.

The flow should be proportional to the square of the diameter and this relationship was used to produce the predicted inlet flows in the previous report.

2. Inlet Flow

The inlet flow was measured using the Venturi meter. These measurements are shown plotted in Figure 4 against the pressure differential across the hydrocyclone. A statistical analysis of the data was carried out and the inlet flow was found to be related to pressure differential by the equation below.

$$Q_i = 14.38 \sqrt{\Delta H + 0.38} \quad \text{--- equation 1}$$

where Q_i = Inlet flow (liters/second)

ΔH = Pressure differential (meters of water)

Figure 4 Inlet Flow

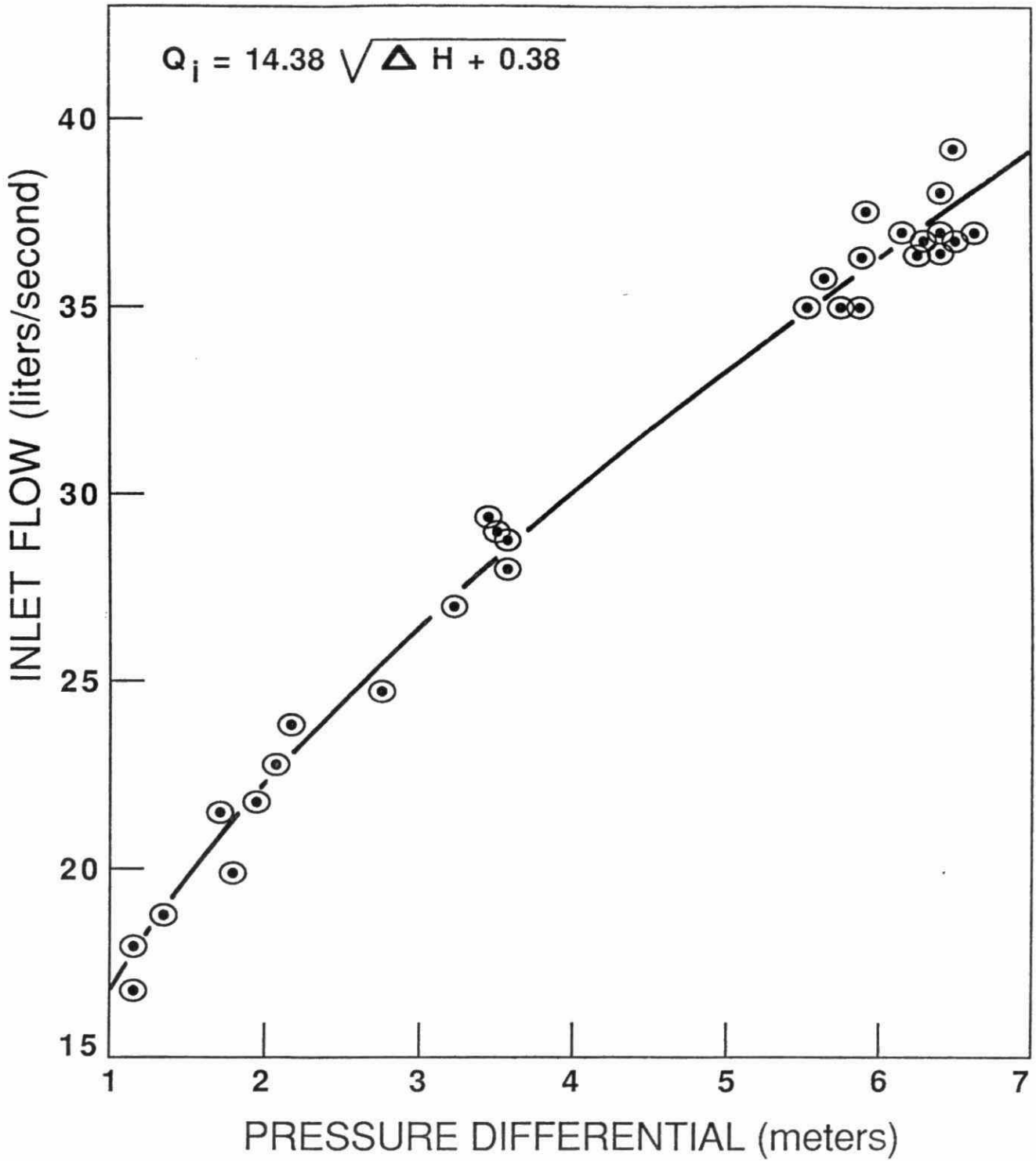
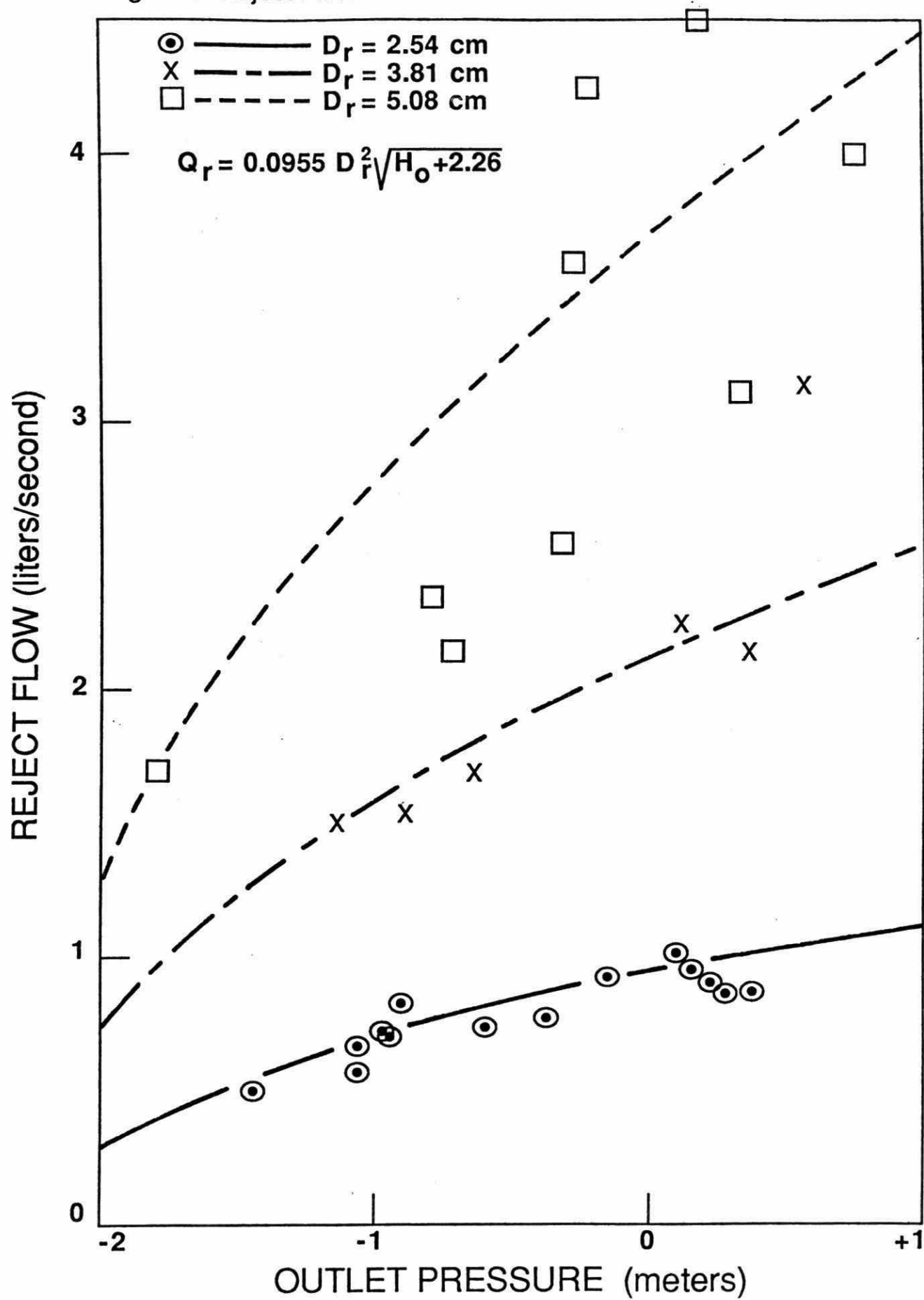


Figure 5 Reject Flow

- 275 -



This equation is shown plotted as the line in Figure 4. The observed flows agree with predicted flows at low pressure but are about 10% low at high pressure differential.

The scatter of observed points about this line is about ± 5 liters/second. An analysis of the effect of other variables such as reject flow, reject orifice size and outlet pressure revealed them as being not significant. The three readings prior to the hydrocyclone oscillated by $\pm 1/10$ meter of water, which also effects flow readings by ± 10 liters/second. Thus variations in flow determinations due to turbulence could well explain the scatters of point about the line. It should be noted that the readings after the hydrocyclone showed very little oscillation. Thus the condition at the pump and turbulence in the pipeline rather than the hydrocyclone lead to the oscillations.

3. Reject Flow

Measurements of reject flow were made by using a stop watch to measure the time to collect $10 \frac{1}{2}$ liters in a pail. The resulted data is shown plotted in figure 5 against outlet pressure with different symbols to show the effect of the use of differing reject orifices. Again, as with inlet flow, the data was subject to extensive statistical analysis to develop the following equation.

$$Q_r = 0.0955 D_r^2 \sqrt{H_o + 2.26} \quad \text{--- equation 2}$$

where Q_r = Reject flow (liters/second)

D_r = Reject orifice diameter (cms.)

H_o = Outlet pressure (meters of water)

This equation is also shown plotted in figure 5 as three lines corresponding to the three sizes of reject orifice used in tests.

The data fits the curve for the 1" (2.54 cm) and the 1 1/2" (3.81 cm) orifice quite well but scatter widely about the curve for the 2" (5.08 cm) orifice. At these high flows the times to fill the $10 \frac{1}{2}$ liters in the pail were between 2 and 5 seconds with possible variation of ± 1 second. Much of this variation was due to observable fluctuation in reject flow which was particularly noticeable with low outlet pressure. An average of 6 readings was taken in attempt to minimize the error in these readings. As will be noted in figure 5 averaging still did not eliminate the scatter about the curve.

Attempts were made to explain these discrepancies by incorporating other variables in the equation. There was a minor tendency for reject flow to be less with higher differential but the effect was not statistically significant.

With normal discharge through an orifice the pressure differential becomes the axial velocity head and the equation for flow becomes

$$Q = C_d A \sqrt{2 g H} \text{ -- equation 3}$$

where Q = flow through the orifice

A = cross sectional area of the nozzle

g = gravitational constant

H = the pressure differential

C_d = a dimensionless discharge coefficient of between 0.55 and 1.0

The value of H for the reject orifice is the $(H_o + 2.26)$ in equation 2, the 2.26 being due to the distance of the reject orifice below the outlet. If one expresses equation 2 in consistent units in the form of equation 3 the value of C_d becomes 0.27 which is ridiculously low. The reason for this is that the throttling in this type of "Vortex Nozzle" (Ref. 8) is through the pressure differential across the vortex which approaches the opening due to centrifugal forces. The rejects issue through the orifice as a hollow cone spray with no fluid in the centre.

The throttling effect of a vortex between parallel plates depends upon the tangential velocity of fluid entering, the density of the fluid and the fluid viscosity as well as the geometry of the system. It has been observed that when this type of nozzle is used in controlling the discharge from hydrocyclones that the reject flow will automatically rise when there is a larger content of oversize solids in the feed. This is the most probable reason for fluctuation in reject flow as the mixer in the centre of the tank may not always blend the accepts and rejects perfectly as they proceed to the tank outlet.

The separating efficiency of the hydrocyclone is dependent upon the percentage rejection, as will be discussed later. This requires use of both equation 1 and 2 incorporated into a new equation

$$R = 100 \frac{Q_r}{Q_i} = 0.664 D^2 \sqrt{H_o + 2.26} / (H_i - H_o + 0.38) \text{ -- equation 4}$$

where R = percent solids rejection

H_i = Inlet Pressure (meter of water)

other terms as previously defined

Solids Removal

1. Theory

Particle removal, in sewage treatment methods, is usually by settling in tanks or clarifiers. One design parameter used is the overflow rate, which can be

expressed as the settling rate of particles which should just be removable at 100% efficiency.

$$S_o = \frac{6Q}{A} \quad \text{--- equation 5}$$

where S_o = settling rate cms/minute

Q = flow cubic liters/second

A = surface area of the clarifier meters²

The efficiency of removal of a particle of settling rate S is then given by the equation below.

$$E(S) = \begin{cases} 100 & \text{for } S \geq S_o \\ 100 \times \frac{S}{S_o} & \text{for } S < S_o \end{cases} \quad \text{---equation 6}$$

Turbulence or thermal currents in a clarifier usually prevent the theoretical efficiency from being achieved.

The literature on hydrocyclones expresses removal capability in terms of the diameter of particle removable at 50% efficiency i.e. d_{50} (Ref. 4). The reason for this is that efficiency versus percent removal curves from experiments are very steep at this point. However, the resulting empirical and also some theoretical (Ref. 9) equations also contain density difference between the particles and that of water and can hence be expressed using Stokes Law as equivalent settling rates of the same particles in still water or S_{50} . The design of hydrocyclones is still not an exact science and there are discrepancies in the equations of various authorities and also with the author's past research. One could, however, express all the design equations for scaling of one design in terms of S_{50} by the equation below.

$$S_{50} = k \frac{D^{n1}}{(\Delta H)^{n2} (R)^{n3}} \quad \text{---equation 7}$$

where S_{50} = settling rate of solids removable at 50% efficiency
D = diameter of the hydrocyclone
 ΔH = pressure differential
R = % Reject rate
 n_1 = exponent between 1 and 3
 n_2 = exponent probably 0.5
 n_3 = exponent probably 0.32
k = a constant dependent upon design proportions

Whereas most theoretical and experimental investigators would agree on the values of n_2 and n_3 indicated above, there is little agreement on the value of n_1 .

Assuming viscous conditions and constant resistance to settling, independent of scale, the $n_1 = 1$. However if settling is impeded by turbulence which is dependent on diameter, the n_1 might be expected to have a higher value, the increase depending upon the design. In the previous reports of References 1 and 2 it was assumed that effect of turbulence would be reduced because of the design proportions and an involute rather than tangential inlet, thus n_1 was taken as 1.

Although Stokes Law may be used to obtain the settling rate of spherical or granular particles it does not apply very well to particle shapes such as fibers or platelets which have a large surface for their mass. The fluid shear and turbulence in hydrocyclones acts upon high surface particles, such as fibres, and sweeps them out of the boundary layer into the inner stream. The use of hydrocyclones to clean pulp suspensions in the paper industry is based upon this effect.

In the author's previous research he used settling tests while using the hydrocyclone to remove silica flour from water. These tests were time consuming but produced a curve of removal efficiency versus settling rate. Equation 6 fitted the experimental data quite well, however, more complex equations which led to a curvature at the top end as efficiency approached 100% gave a better fit. Unfortunately, because of the delay in the installation of the equipment and difficulty in obtaining research assistants after classes began, it was decided not to use this time consuming technique.

2. Grit Separation

A fine grade of sand was used for grit tests with a mean particle size approximately 100 microns. Samples of 10 1/2 liters volume were taken of feed to and accepted fluid from the hydrocyclone during its operation. These samples were then washed through 100, 200 and 320 mesh screens. The sand on the 200 & 320 mesh screens was determined by washing them onto a filter paper which was then dried and weighed. The results of these experiments expressed as percentage of sand removed are shown in Table 1. The equation 7 shows that

Table 1
Grit Removal $D_r = 2.54$ cm

Feed Concentration (100 - 200) mesh = 904 p.p.m.
(200 - 300) mesh = 104 p.p.m.

ΔH	R	E%		$\sqrt{\Delta H} R^{0.32}$
		100 μ	60 μ	
(meters)	%	100-200	200-320	$\sqrt{\text{(meter)}}$
6.43	1.76	99.96	96.64	3.04
6.24	2.09	99.98	99.94	3.16
5.86	2.41	99.94	99.20	3.21
3.44	1.94	99.94	97.84	2.29
2.04	3.77	99.76	93.39	2.18
1.15	5.21	99.60	91.70	1.82
1.78	2.60	99.30	91.10	1.81
		s=60	s=20	
		cm/min	cm/min	
		d=100	d=60	
		microns	microns	

the pressure differential and percentage rejection are the important factors controlling the size of grit removable, i.e. S_{50} , and these factors are included in the table together with the function $\sqrt{\Delta H} R^{0.32}$ which is from equation 7. It was found that the sand on the 100 mesh screen had a mean particle size of 100 microns and should hence settle at a velocity of 60 cm/min and that the sand on the 320 mesh screen had a mean particle size of 60 microns and settling rate of 20 cms/min.

The hydrocyclone proved capable of virtually 100% removal of both grit sizes. The material left on the filter from the accepted sample appeared in most cases to be traces of paper fiber which may have been left in the casing of the pump and corners of the tank from their last usage.

We may hence say that since the 320 mesh sand is virtually 100% removed that the S_o for this equipment on sand is less than 20 cm/min and that the S_{50} is less than 10 cm/min.

The predicted value from the previous report (Ref. 2) was a value of the order of 5 cm/min for S_{50} with a pressure drop of 6 meters of head and 10 cm/min for a pressure drop of 1.5 meters of head. This is not in conflict with the observation in Table 1.

3. Sawdust Separation

It was decided to do tests on removal of an organic material for two reasons:

- a. To have some idea of capability of removing organics from sewage
- b. To attempt to obtain an efficiency versus settling rate data, using screen analysis to separate sizes.

When attempts to obtain samples of granular plastic powder failed, the author was forced to fall back on the use of sawdust.

Bags of sawdust were obtained from a local lumber dealer and screened to obtain the finest materials which would pass through a 60 mesh screen. This fraction, which was only 10% of the sawdust, was then put in water and boiled to remove any air which would make it float. The wet sawdust was washed to remove resin then used in the tank for removal tests.

The laboratory procedure was similar to that used for the grit except that a 60 mesh screen was used above the 100 mesh screen. The results of these tests are shown in Table 2 together with the pressure drop, percent reject rate and their combined function.

In order to express the screen mesh sizes or settling rates the density of the wetted sawdust particles was measured, using a picnometer, to yield a density of 1.1378 grams per ml. The net density of 0.1378 was then used with Stokes Law to give settling rates. The mean diameters of the various mesh fractions, their mean concentration in the feed and the expected settling rate of this material are shown at the top of Table 2.

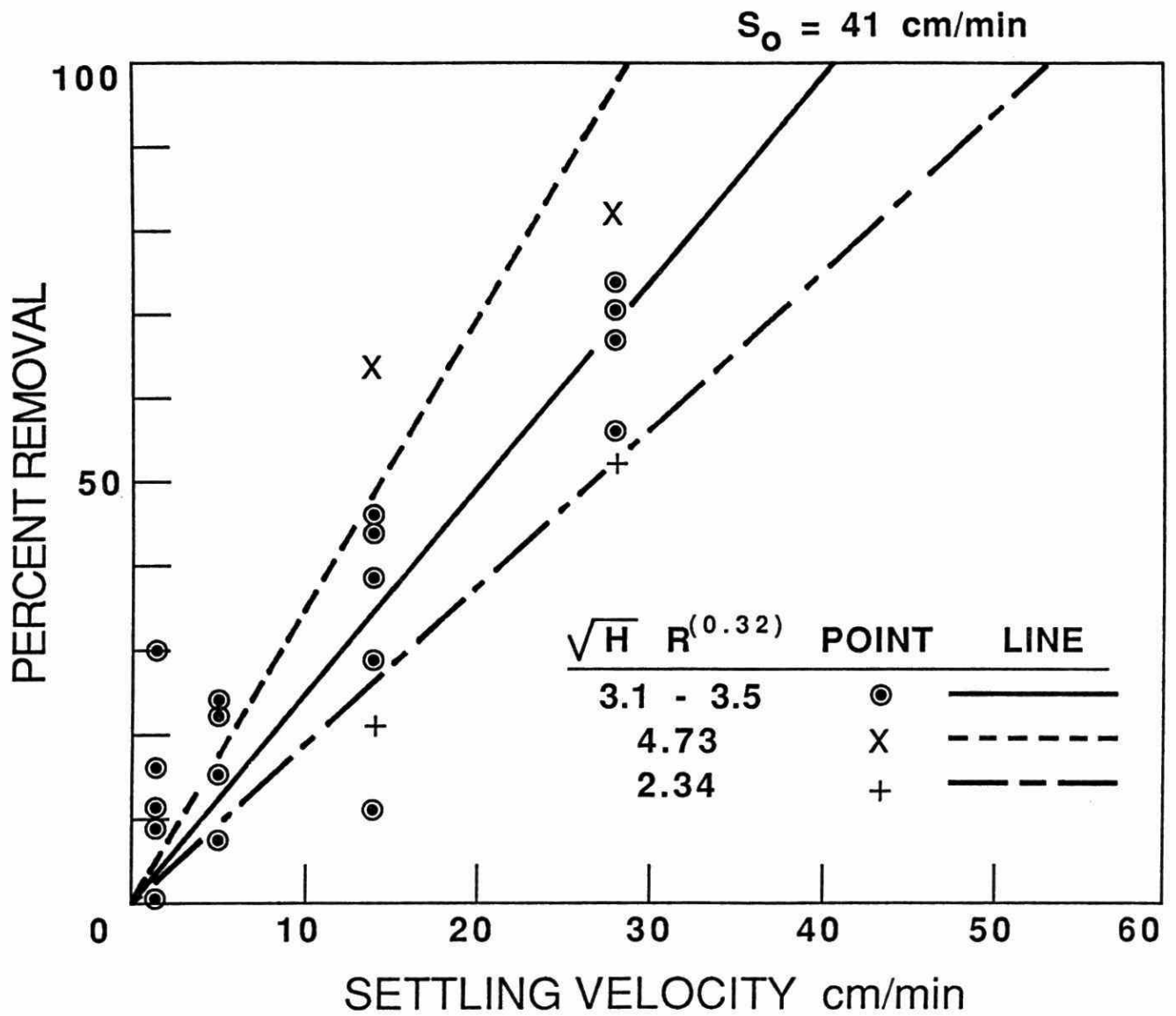
Table 2

Sawdust Removal D = 2.54, 5.08, 3.81

Feed Concentration 60 mesh = 35 p.p.m.
 100 mesh = 133 p.p.m.
 200 mesh = 132 p.p.m.
 325 mesh = 33 p.p.m.
 Overall = 333 p.p.m.

Δ (meters)	R (%)	E%					$\sqrt{\Delta H} R (.32)$
		60	100	200	325	All	
6.40	1.98	0	44.5	15.2	0	26.5	3.15
5.86	2.58	67.8	44.0	7.2	11.3	30.6	3.28
5.57	8.8	81.7	54.0	31.3	31.9	48.0	4.73
2.167	14.9	90.8	27.8	2.6	0	31.3	3.49
5.73	6.1	72.5	38.5	32.5	30.0	39.0	4.26
3.56	5.7	55.9	38.4	22.8	9.8	30.52	3.29
5.86	2.5	70.5	28.9	23.8	16.6	29.0	3.28
5.86	2.58	73.7	10.3				3.28
2.74	2.95	52.8	21.6				2.34
<u>6.62</u>	<u>4.58</u>	<u>79.2</u>	<u>42.4</u>				<u>4.19</u>
S	cm/min	28	14	5	1.5		
d	micron	250	176	100	55		

Figure 6 Efficiency in Removing Sawdust



There were 5 tests in which the separation product lies between 3.1 and 3.5 and the separation efficiency on the screen factors in these tests was plotted against the settling rates of the factors in Figure 6. These points, although showing considerable scatter, lay on a reasonable straight line in the form of the clarifier efficiency, i.e. equation 6. The condition with highest reject rate pressure product of 4.73 and lowest product of 2.34 are shown as other lines in Figure 6.

The value of S_0 from this graph, i.e., the 100% intercept, varied from 29.5 to 58.3 cms/min with the majority of test at 41.3 cms/min. This is much inferior to the results from grit tests which gave complete removal of grit with a settling rate of 20 cms/min. Close examination of the wetted sawdust showed that the particles were not granular but the majority were little flat chips with fragmented ends. The discrepancy is hence likely due to particle shape and removal efficiency of granular shaped organic particles would be higher.

4. Removal of Vegetable Washings

The liaison officer for the Ministry, Mr. Henry Kronis, arrived on Sept. 11 with a bag of vegetable washings for study. The sawdust had been cleaned out and this material was added to the tank. The vegetable washings consisted of black granular material, fibrous material and some slimy gelatinous material. Rejects from the hydrocyclone were very black but settling in Imhoff cones of feed and accepts showed only a small difference in settled volume. However these results may have little meaning as the fibrous and gelatinous material has great bulk, hence volume, and would not be removed. Attempts to filter the normal 10 1/2 liters of the feed led to blocking of the filter by the slimy material present. The sample sizes for filtrations were hence reduced to 500 c.c. with the results given below.

Test on September 11 Table 3

Sample	Concentration p.p.m.	Efficiency %
Feed	590	
Accept 1	362	38.6
Accept 2	352	40.34

The following day a 2" orifice was inserted to control reject flow and the hydrocyclone operated as follows.

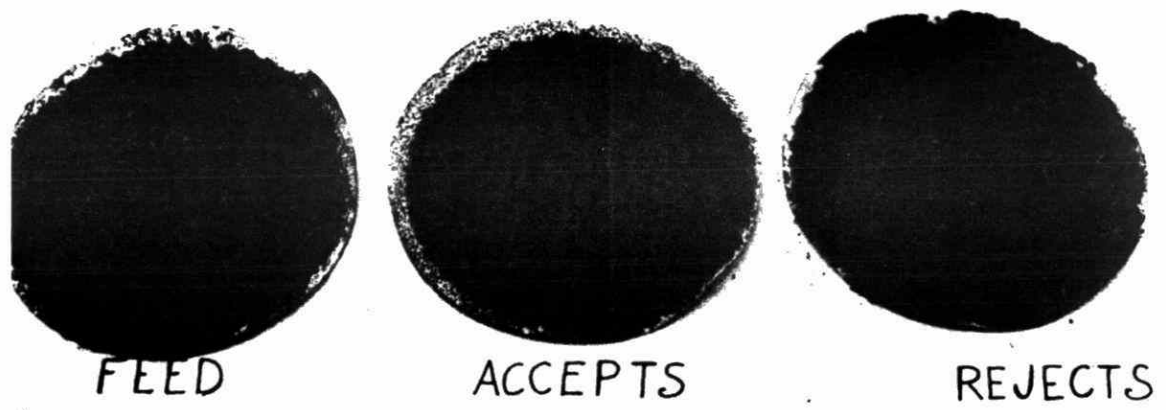


Figure 7 Filter Pads of Vegetable Washings

Pressure drop = 6.15 meters
Inlet Flow = 37 liters/second
Reject Flow = 4.25 liters/second
Rejection % = 11.486
Reject orifice = 2 inches or 5.08 cms

Samples were taken of feed accepts and rejects with results as follow:

<u>Test on Sept. 12 Table 4</u>		
Sample	Concentration	Efficiency
	p.p.m.	%
Feed	1746	
Accept	332	80.9
Rejects	5458	63.94

These results show much better performance than the previous day and, to show the character of materials in these filter pads and confirm this effective removal, they were photographed as shown in Figure 7.

Although the solids content of the three accepted samples are similar in the two days, there is a great discrepancy in the concentration in the feed sample. Efficiency can also be calculated by using the solids in the accepts and rejects, with their due proportion, to calculate a new feed and hence efficiency. This figure is shown on the rejects line of the results of September 12.

It would appear that there is a wide variation in the solids content of the feed with the use of a 500 c.c. sample. This is probably due to the imperfect blending of accepts and rejects by the stirrer as they proceed to the outlet. Hence the efficiency of 64%, calculated from accepts and rejects concentrations, is probably closest to the real efficiency. The calculated feed concentration from the joining of these two concentrations is 920 parts/million.

Further tests may be run on vegetable washings if the exact removal is important to a possible test of the hydrocyclone at Bradford.

Discussion and Conclusions

1. From experiments

The 25 inch hydrocyclone proved capable of handling a flow of 36.4 liters/second at a differential of 6 meters (or 600 US GPN at a differential of 20 feet). The inlet flow was not effected by the reject orifice size or outlet pressure, but by the differential only, according to an equation established by statistical analysis.

The reject flow was varied in experiments from 0.5 liters/second to 5 liters/second and was found to be dependent upon the reject orifice size and outlet pressure according to an equation also established by regression analysis. The percentage rejects can be obtained by use of both regression equations, equation 4, or the graphs, Figures 4 and 5.

The hydrocyclone proved capable of removing virtually all grit 60 microns in diameter or larger. It is believed that the unit may be able to remove 50% of grit which settles at a rate of 5 cm/minute.

The hydrocyclone separated fine organic matter, such as sawdust. It removed well over 50% of 60 mesh sawdust and 64% of the solids from vegetable washings. However, although granular shaped particles can readily be removed, fibers and large thin particles such as fruit and vegetable skins may be difficult to remove. Nevertheless the hydrocyclone has sufficient separating capability to be considered as a potential substitute for primary clarifiers. Overflow rates expressed as settling velocity for various devices are shown below in Table 5. It should be noted however that the velocity from the hydrocyclone has been established from experimental measurements, whereas the others are obtained using equation 5.

Separation Comparison Table 5

Device		Overflow rate cm/min.	m ³ /m ² .day
Primary Clarifier	=	1 - 12	14 - 170
Hydrocyclone	=	10 - 40	140 - 570
Grit Channel	=	50 - 100	720 - 1440
Swirl Chamber	=	200 - 300	2880 - 4320

The hydrocyclone was designed with a high orifice ratio, i.e. smaller inlet and outlet sizes and hence lower flow for a given diameter. Whereas this might lead one to think that the unit tested would be uneconomic, since it would only handle about half the flow of a 25 inch (63.5 cm) unit of conventional design, this is false logic since one should only compare units which have similar separation capability. Based upon the author's own test data and promotional sales data on commercial hydrocyclones it would require a bank of 15 to 25 6 inch or 8 inch (15 - 20 cm) units to produce the separation capability and flow as obtained in these tests. These units would have small openings and would plug frequently from foreign objects in sewage. The author does not have financial data but it seems obvious that an installation of 15 - 8" hydrocyclone with headers, etc., should be much more expensive than one of the units under test.

2. Design

Experiments seem to have confirmed design prediction on hydraulics very well and have apparently also confirmed predictions on separation capability if one allows for the effect of shape.

It should hence be possible to extend the theory of scaling to produce other sizes of units in the same design proportions with reasonable confidence. The removal capability is probably much greater than needed for simple grit removal and a much larger unit with hydraulic capacity going up as the diameter squared would probably give adequate separation of grit. A unit 6 feet in diameter operating at 6 meters of head differential could probably handle 300 liters/second, and remove over 90% of 100 micron grit.

An alternative, for grit removal only, would be to increase the size of inlet and outlet passages to enable the 25 inch unit to handle a flow of 80 to 90 liters/second, at 6 meters differential, reducing the efficiency on 100 microns grit to approximately 90% efficiency from the existing 100%.

Better removal of organics would have been obtained by operating the existing design at a high pressure differential. It is designed to be able to withstand a static pressure of 25 p.s.i. and could hence be operated safely with this same differential, which would be 17 1/2 meters of water. The inlet flow, according to equation 1, would be 60.8 liters/second and the effective overflow rate as low as 6 cm/minute.

The unit is made of mild steel and is hence only suitable for a short test period, due to corrosion. In practice the corrosion problem may be overcome by rubber coating, as practiced by many manufactures of hydrocyclones for metallurgy, or of stainless steel or plastic as used in the paper industry. Very large units might be made of reinforced concrete with a ceramic lining.

3. Installations

It will usually require a bank of units to handle the sewage flow in a sewage plant. The number of units to be installed will depend on the maximum flow to be handled and the maximum pressure differential to be used in operation.

The hydrocyclones may be supplied either by gravity differential or by a pump. For pump supply, the best arrangement would probably be with the unit elevated and the outlet discharging to a high level between the accept and reject outlet, thus causing a slight vacuum at the outlet. For gravity operation the unit would need to have the inlet and outlet below the feed level and positioned such that the outlet flow discharges to a level somewhat between the accept and reject outlet.

The hydrocyclone can be operated with a broad range of pressure differentials and outlet pressures. However continuous operation is desirable as it requires several times the volume of the hydrocyclone to build up the velocity pattern, whereas on shutdown the contents all drain out through the rejects exit. A gradual build up of flow on start up and reduction in flow,

such as achieved in slowly opening and closing a valve in the inlet line, is desirable to avoid water hammer effects.

Some form of automation may be necessary to look after the wide swing in flows normal to sewage plants. In a system with multiple primary units this may be looked after by shutting down numbers of units, by recirculating accepted flow for retreatment to keep the full system in operation or by varying the feed pressure. In a gravity feed system it may be possible to control the number of units in operation by allowing the level in the feed box to vary and having outlets from it to hydrocyclones at different levels. In systems with multiple pumps each pump could feed separate hydrocyclones units or banks of units.

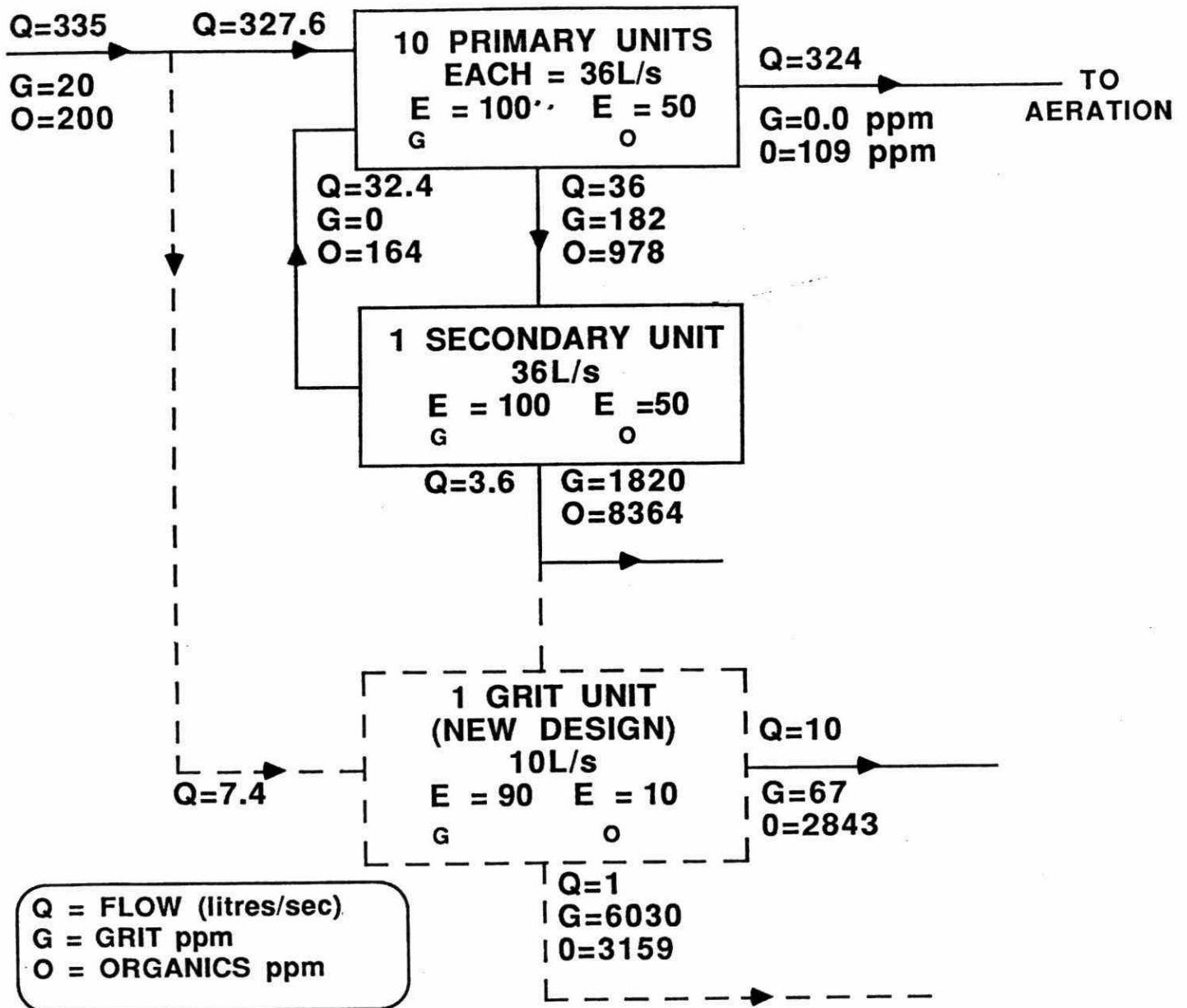
Every system must have a method of looking after the rejects from the primary bank of hydrocyclones. The system of secondary and tertiary banks of units used in the paper industry may be employed for this purpose. Figure 8 shows a flow chart showing how a system employed in place of a primary clarifier might operate. The logic of the system is also described below.

A. The system is designed to handle a maximum flow of 335 liters/second and it is assumed that the sewage contains 200 p.p.m. total organics and 20 p.p.m. grit. The primary system, consisting of 10 of the units tested operating at 6 meters of differential, handles 360 liters of input, rejects 10% of its input with 50% removal of organics and 100% removal of grit. The accepted flow of 324 liters/second goes to the aeration tank for secondary treatment while the rejects go to a secondary unit. The feed to the primary consists of the input plus the accepted flow from the secondary.

B. The secondary unit, of the same design, also operates at 6 meters of differential and 10% reject rate. It also would remove 100% of the grit, but since the organic is all the coarser material, it may remove 85%. The accepted flow would be returned for retreatment in the primary. The reject flow of 3.6 liters/second would have a grit concentration of 1,820 p.p.m. and organic content of 8,364 p.p.m. This material may then go to some thickening device and digestion.

C. It may be desirable to separate the grit from the organics in a third stage hydrocyclone. This would need to be a unit of lesser separating capability, by both design and operating pressure. It might be possible to obtain such a unit with 10% capability in removing the organics but 90% in removing grit. It would be necessary to dilute the rejects from the secondary with raw sewage to have sufficient flow to use a large enough unit that it would not block. The accepted flow of 10 liters/second would have only 67 p.p.m. of grit but 2,843 p.p.m. of organics and could be sent to some thickening device. The reject flow of 1 liter/second would have 6,030 p.p.m. of grit and 3,159 p.p.m. of organics. The latter organics would probably be

Figure 8 A Hydrocyclone System Schematic



coarser granular material such as coffee grounds or seeds which do not putrify and could go directly to landfill.

In a larger system, a third stage unit of high enough capacity could be used to build up final solids content in rejects to 2 to 3% solids (20,000 - 30,000 p.p.m.).

4. Application of Hydrocyclones

The hydrocyclone is a tool which has potential for use in environmental treatment in various roles, provided units are designed appropriately for the service.

The removal of grit is excellent and units could be employed either before or after screening to achieve superior grit removal. I would be preferable to use the hydrocyclones after screening to prevent possible blockage.

It is also possible to use hydrocyclones in place of primary clarifiers. It is particularly effective in removing granular materials and would be effective in such particles as sawdust, coffee grounds, seeds and undigested hard food particles such as corn kernels and nuts. The fluid shear would probably separate gas bubbles from particles which sometimes prevents settling in primary clarifiers.

However, separation in hydrocyclones is influenced by particle shape and particles with a large surface, such as fibres and skins, would be difficult to remove. Flocs of alum or ferric oxide from use of flocculents have large surface and would not be removed. On the other hand organic flocculents produce tighter flocs which might be removed by hydrocyclones.

The effect of replacing primary settling with hydrocyclones on the activated sludge process that follows is uncertain. We can speculate on the possible effects of removing granular particles but permitting fibrous and other high surface particles to pass on to the aeration tank. Microscopic examination of activated sludge usually shows that all fibrous particles are usually enclosed in colonies of bacteria. They may have the effect of producing a better settling sludge in the secondary clarifiers and thus permitting the process to run at a higher food to microorganism ratio.

In more recent years, municipal stormwater has been considered as contributing to environmental contamination. However, treating the entire volume of stormwater in sewage treatment plants raises difficult problems. One solution would be to pass the stormwater through an efficient hydrocyclone, with the reject portion being sent to sewage treatment.

Hydrocyclones may also be applied to solve pollution problems from industrial waste, by local treatment.

Although the research discussed here involved using hydrocyclones to remove particles denser than water, the author has also done research on use of hydrocyclones to remove oil and floating material from water. A copy of a report dealing with recent studies in this area will be sent to the liaison

officer along with the report.

Recommendations

The hydrocyclone has performed well in pilot plant trials and is now ready for field trials.

The decision as to the location and nature of the field trial is one that must be made by the Ministry. The author would like the trial to be one where the equipment would be tested as a substitute for primary treatment. One form of application is where a plant is faced with treating an industrial waste which has fine granular material. The material from Bradford is an example of the type of problem where a hydrocyclone would be particularly useful. If further tests are needed to reach this decision, it would be preferable that they be carried out before May 1987, since next summer the Civil Engineering Department plans to make changes in the corner of the laboratory where the hydrocyclone pilot plant is located.

The original budget allowed funds for revision of the equipment after pilot studies and before field trials. Two such alterations might be rubber coating of the interior to reduce both abrasion and corrosion and construction of the curved cone and longer barrel alternative design shown in the original drawings. The decision on these matters will wait until the Ministry has read this report and made their recommendation as to what changes might be made.

References

1. Boadway, J.D. "A Low Pressure Hydrocyclone for Grit Removal", A report written for the Ministry of Environment.
2. Boadway, J.D. "A Hydrocyclone Designed for Energy Recover", A progress report written for the Ministry of Environment.
3. Boadway, J.D. "A Hydrocyclone Designed for Energy Recovery", A second Progress Report on Project No 184 PL.
4. Bradley, D. "The Hydrocyclone", a text published by Pergamon Press in 1965.
5. Freeman, H. and Skelton, Pulp and Paper Magazine of Canada 38 No. 2: 170-171, 188 (Convention issue 1937).
6. Hammer, Mark V. "Water and Wastewater Technology" page 355.
7. Field, Richard "The Dual Functioning Swirl Combined Sewer Overflow Regulator/Concentration", U.S. Environmental Protective Agency report PB-227-182, Sept. 1973.
8. Boadway, J.D. "Vortex Nozzles for Limitation of Discharge Rates", The Canadian Journal of Chemical Engineering Vol. 51, February 1973.
9. Medronho, R.A. and Svarovsky, L. "Tests to Verify Hydrocyclone Scale-up Procedure", Second International Conference on Hydrocyclones, Bath, England, Proceedings pages 1-14 (Sept 1984).

UPPER HUMBER RIVER
WATER QUALITY STUDY

TECHNICAL REPORT #8

A REPORT
OF THE

TORONTO AREA WATERSHED
MANAGEMENT STRATEGY
STEERING COMMITTEE

Prepared by:

Brian A. Hindley
Richard P. Hubbard
Stephen H. Maude

The Metropolitan Toronto and Region
Conservation Authority
5 Shoreham Drive
North York, Ontario
M3N 1S4

December, 1985

TABLE OF CONTENTS

Abstract

1.0 Introduction

2.0 Methods

- Study Area
- Surface Water Quality
- Bed Sediment Sampling
- Overland Sediment Delivery
- Field Inventory

3.0 Results

- Synoptic Survey
- Event Sampling: Comparisons to Water Quality Objectives
- Parameter Correlations
- Description of Wet Event
- Subbasin Chemical Loadings
- Bed Sediment Chemistry
- Land Use
- Overland Sediment Delivery
- Field Inventory

4.0 Discussion

5.0 Conclusions and Recommendations

- Conclusions
- Recommendations

6.0 Literature Cited

Abstract: During the course of the Toronto Area Watershed Management Strategy Study (TAWMS) it became apparent that violations of the Ontario Ministry of the Environment's Provincial Water Quality Objectives (PWQO) routinely occurred in the Humber River north of the Metropolitan Toronto boundary. This one year study was conducted to better identify and characterize the main sources of selected pollutant loadings within the predominantly rural Upper Humber River watershed. Grab samples were collected during three dry event periods between July and December 1984 as well as intensive sampling during one storm event which occurred in late fall. Fecal coliform geometric mean densities during dry weather indicated water quality degradation throughout the Upper Humber watershed, even at stations relatively close to source. Dry weather concentrations of other parameters including TSS, TP, Cu, Pb, and Cd were also in exceedance of PWQO at stations throughout the study area. Exceedances were particularly frequent between the towns of Bolton and Woodbridge. Identified point source inputs as well as stretches of severe streambank erosion and cattle access were all likely contributors to the observed parameter levels. The lowest dry weather concentrations generally occurred in December suggesting a strong seasonal influence. With some exceptions (notably Cu and Pb), parameter concentrations were greatest under wet weather conditions. Physiographic differences between subbasins, influencing both parameter concentrations and loadings during the storm event, were observed and are discussed in the report. The study concludes that water quality problems on the Upper Humber watershed, although not of the magnitude of those occurring in the lower Humber, cannot be discounted in the development of a water management strategy if PWQO are to be achieved.

1.0 Introduction

The Toronto Area Watershed Management Strategy Study (TAWMS) was initiated in response to concerns expressed by the Metropolitan Toronto and Region Conservation Authority (MTRCA) and its member municipalities regarding the extent of water quality degradation in the watercourses and the lack of information on pollutant sources and remedies.

The purpose of the TAWMS study is to identify pollutant sources within the watersheds and develop a comprehensive water management plan which incorporates cost effective measures for improving water quality, and an implementation strategy which outlines agency responsibilities and time frames for improvement measures.

The five-year study emphasized the Mimico Creek, Humber and Don River watersheds since these typify the wide range of water quality problems experienced by all watersheds within the MTRCA jurisdiction. After an initial screening study in 1981, the TAWMS work schedule was to concentrate first on the Humber River and then develop strategies for the Don River and finally Mimico Creek.

Because of the complexity and greater significance of urban water quality problems and because of funding restraints, the intensive study of the Humber River in 1982 was limited to the watershed area within the Metropolitan Toronto boundaries. The study was again limited to the lower Humber River in 1983 when the resolution of water quality problems along the Metropolitan Toronto waterfront was added to the terms of reference for the TAWMS study.

As a result of detailed pollution studies on the lower Humber River from 1982-83, it became apparent that violations of the

MOE's Provincial Water Quality Objectives (PWQO) in the Humber River occurred north of the Metropolitan Toronto boundary. Therefore, in order to address the TAWMS objective of restoring water quality to PWQO, the incorporation of corrective measures in the Humber River north of the Metropolitan Toronto boundary was necessary as part of the overall strategy. Specifically, exceedances of fecal coliform bacteria (FC), total phosphorus (TP), total suspended solids (TSS), lead (Pb), cadmium (Cd) and copper (Cu) were of concern in the Upper Humber watershed (TAWMS 1984).

Accordingly, in 1984, the MTRCA submitted a proposal to the MOE and received a grant to address these concerns in the Upper Humber watershed. The specific objectives of this study were as follows:

1. To evaluate the contaminant contributions of Upper Humber River subbasins by sampling surface waters for selected chemical and microbiological parameters in dry and wet weather.
2. To sample the bed sediment of these same subbasins in order to obtain a more historical perspective on contaminant contributions.
3. To map areas of potentially high overland sediment delivery in rural areas of the watershed using an adaptation of the Universal Soil Loss Equation.
4. To identify and describe land use problems (e.g. livestock access), point source inflows and stream bank erosion sites by inventorying watercourses of the Upper Humber River watershed.

2.0 Methods

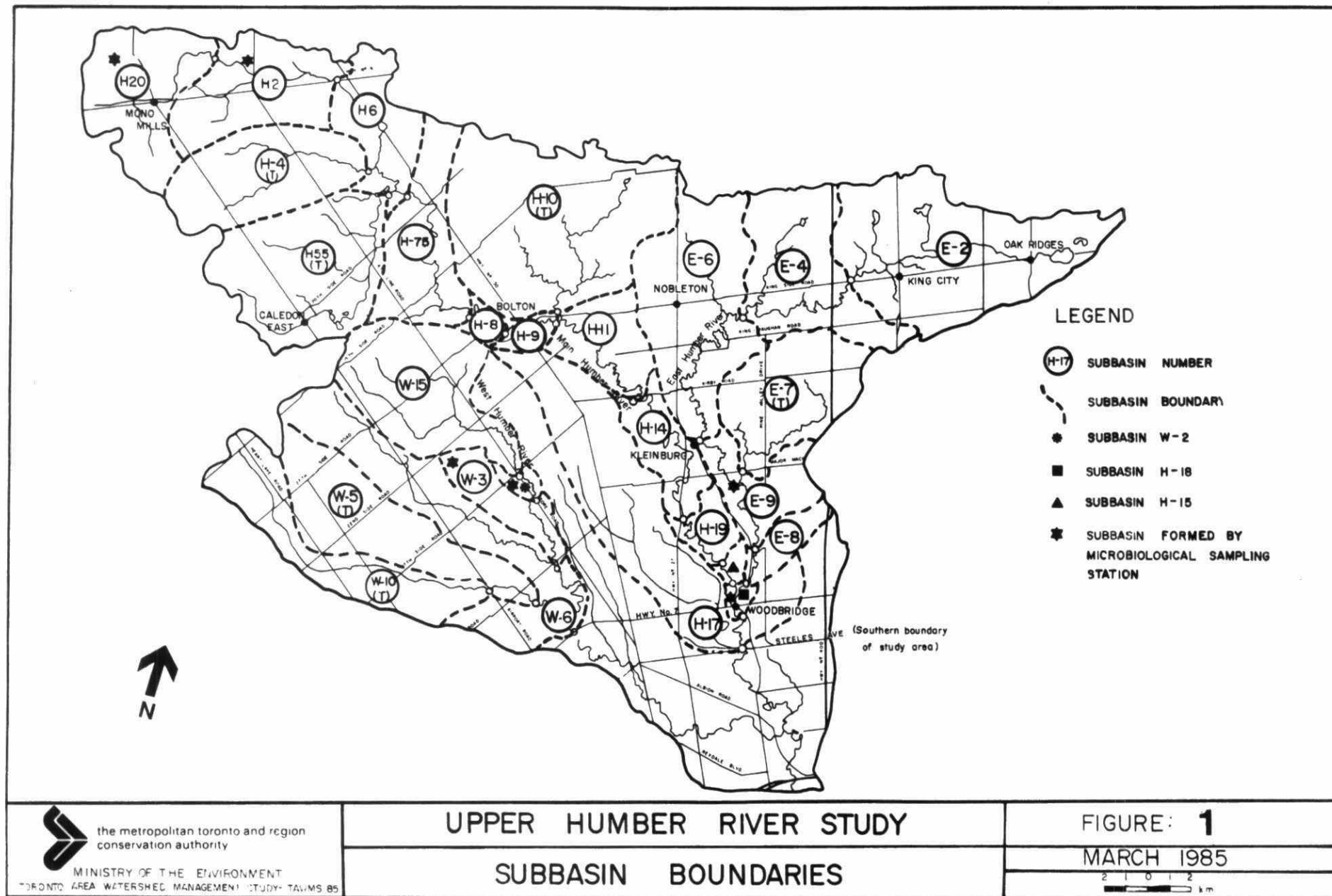
Study Area

The study area comprises 700 km² of the Humber River watershed north of Steeles Avenue, the Metropolitan Toronto boundary (Figure 1). The watershed is bounded by the communities of Oak Ridges to the northeast and Mono Mills to the northwest and is formed of three main rivers: the Humber, East and West Humber Rivers. Within the boundaries of the study area the Humber River is the largest of the three with a watershed area of 346 km². The East and West Humber Rivers have watershed areas of 190 and 160 km² respectively. Average stream gradients range from 1% in the upper reaches to 0.2% further downstream.

The study area is predominantly rural. The rural component (including areas of open space and forested lands) comprises about 97% of the watershed. Urban development is primarily restricted to several small communities found throughout the study area including Bolton, Nobleton, Woodbridge and Kleinburg.

Surface Water Quality

To assess the relative pollutant contributions of Upper Humber River subbasins a surface water quality monitoring network was established. Water quality sampling stations were set up at intervals along the Humber, East Humber and West Humber Rivers, and near the mouths of any major tributaries. Land use in the watershed was taken into consideration in the selection of the stations. For example, sampling stations were established to evaluate the effects of agricultural versus forested subbasins. Other stations were located upstream and downstream of urbanized areas such as the towns of Bolton and Woodbridge.



Synoptic Survey

Initially, 30 microbiological and 30 chemical stations were sampled synoptically to obtain some indication of where problem areas might exist. One sample for chemical analysis was taken from each station on June 20, 1984. Microbiological samples were taken daily from each station from June 20 to 22, 1984 inclusive.

Dry Event Sampling

Event sampling stations were selected based on the results of the synoptic survey. Although several new stations were created, the total number of sampling stations was reduced to 21 for microbiological sampling and 19 for chemical samples (Figure 1). Stage discharge curves were established at all chemical sampling stations from existing Water Survey of Canada (WSC) gauges or by installing staff gauges and monitoring flows. Three dry events were sampled between July 23 and December 13, 1984: Dry Event 1 from July 23 to 27, Dry Event 2 from August 27 to September 5, and Dry Event 3 from December 10 to 13. Dry event sampling consisted of taking chemical samples daily for three consecutive days (four days for Dry Event 2), and microbiological samples daily for five consecutive days (four days for Dry Event 3). At least two rainfree days were necessary prior to initiation of dry event sampling. Once sampling for a dry event had begun, however, precipitation could potentially interfere with the dry conditions. Dry Event 1 was completely free from rain. During Dry Event 2 it rained heavily prior to sampling on the third day. Therefore, sample days four and five were postponed until the following week after another two rain-free days had passed. An extra day of chemical sampling was added at this time. Rain also occurred just prior to the fourth day of sampling in Dry Event 3. These rain disturbances were taken into account in interpreting the dry weather data as outlined subsequently.

Wet Event Sampling

Wet event sampling was undertaken from November 11 to 14, 1984. Three intense, short-duration rainfalls on November 9 and 10 preceded a major rain storm which occurred from late November 10 to November 11. For most stations, water samples were collected at 90-minute intervals throughout the initial runoff event.

At each chemistry station, river stage was recorded on every sampling occasion and a hydrograph was plotted. This hydrographic information was used to select about 6 samples from each station for analysis. For the tributary stations, H-4(T), H-55(T), H-10(T) and E-7(T), chemical samples taken throughout the initial runoff period were composited flow proportionately (Baun 1982).

Subsequent to the intensive sampling, additional samples were taken over the next three days as the rivers gradually returned to near base-flow conditions.

Sample Analysis

Water samples were analysed primarily for TSS, TP, Cu, Pb, Zn, Cd, FC, EC, FS and PA using standard MOE methods (MOE 1981). Sample analysis for Dry Event 3 was carried out by the Laboratory Services and Applied Research Branch of the MOE. All other samples were analysed by BEAK Consultants Ltd., by staff familiar with MOE analytical methods. We feel that some discrepancies in results obtained by the two laboratories may have occurred, particularly in the case of trace metals.

Bed Sediment Sampling

Bed sediment samples from 19 water chemistry stations were collected from November 20 to December 3, 1984. At each site, a composite of 3 samples was collected at river bends or where decreases in water velocity had permitted deposition of fine textured sediments. Samples were analysed for grain size, total phosphate, copper, lead, zinc and cadmium.

Overland Sediment Delivery

Sediment loading from rural overland sources was mapped using a methodology developed by the Lands Directorate at the Canada Centre for Inland Waters (CCIW) (Snell 1984). This methodology, an adaptation of the Universal Soil Loss Equation, utilizes a series of map overlays to target areas contributing significant overland sediment volumes to watercourses. While this technique does not quantify sediment inputs, it does allow for the setting of priority areas for management.

Field Inventory

A field inventory was conducted from June to October, 1984 in an effort to locate potential pollution sources. Two person crews walked watercourses of the Upper Humber system, noting problem land uses (e.g. areas where livestock had free access to the watercourse), point source inflows, and stream bank erosion sites. These features were described using standardized forms and their locations were indicated on topographic maps (1:25,000 or 1:50,000 scale).

3.0 Results

Drainage areas were planimetered for comparison to water chemistry loading calculations. Approximate areas for the 18 "chemistry" drainage basins are as follows:

1.3 - 10ha	H-15, H-9
10.1 - 30ha	H-14, H-11, H-4(T), E-8, W-10(T)
30.1 - 50ha	H-75, H-55(T), E-7, E-6, W-5(T), W-15
50.1 - 95ha	H-17, H-10(T), H-6, E-4, W-6

Locations of subbasins are shown in Figure 1.

Synoptic Survey

Fecal coliform analyses indicated fairly widespread exceedances of the Provincial Water Quality Objective of 100 counts/100 mls. Geometric mean densities ranged from 40 to 2,113, occurring at stations W-8 and E-8 respectively. The geometric means exceeded the objective at 19 of 30 stations. On the West Humber and Humber Rivers, exceedances occurred at 38% and 64% of the sampling stations respectively. All but one (88%) of the stations on the East Humber exceeded the objective. Escherichia coli densities closely paralleled those of fecal coliform bacteria.

The Provincial Water Quality Objectives (MOE 1984) state that when pathogenic organisms such as Pseudomonas aeruginosa can be enumerated and frequently isolated from water, a potential health hazard exists. Geometric mean densities of P. aeruginosa (PA) ranged from <2 which occurred at several stations to 12 on the West Humber at Highway 7 (W-6) and 10 on the Humber River at Steeles Avenue (H-17). The greatest densities generally occurred on the Humber River south of the community of Kleinburg.

Based on these results, some sampling stations were eliminated and others shifted to more adequately sample problem areas.

Concentrations of the nitrogen parameters (ammonia, total kjeldahl, nitrate and nitrite) were never in exceedance of suggested water quality guidelines. Similarly, zinc levels were well within the MOE objective of 0.05 mg/l at all stations. Based on these results samples were not analysed for the above parameters during the remainder of the study.

Total suspended solids exceeded the guideline of 25 mg/l (McNeely et al. 1979) at 12 of 30 stations. On the East Humber, the highest level (48 mg/l) was found at station E-8 near Woodbridge. On the West Humber the greatest concentration (98 mg/l) was found at station W-5(T) located on a tributary in the southern portion of the watershed. The highest overall TSS concentration of 124 mg/l was found at station H-14 on the Humber River. All five exceedances occurring on the Humber River were in the southern stretches of the watercourse.

Total phosphorus concentrations exceeded the guideline of 0.03 mg/l at 27 of 30 stations. Values ranged from 0.024 mg/l at E-8 and H-10(T) to 0.132 mg/l at H-14. The highest concentrations were found on the southern stretches of the Humber River above the town of Woodbridge.

Trace metal analyses for Cu, Pb and Cd revealed that wide-spread exceedances occurred only with Cu. Violations of the MOE objective occurred at 25 of 30 stations. Concentrations ranged from 0.003 mg/l at station H-4(T) to 0.021 mg/l at W-7(T). Although elevated Cu levels were found at W-7(T), the station was eliminated because of extremely low base flows and the strong likelihood that the tributary would become dry during summer periods. Analyses for Pb were maintained through the study because Pb concentrations were uniformly close to exceeding the objective throughout the watershed.

Event Sampling: Comparisons to Water Quality Objectives

At each sampling station, for each event, exceedances were considered in two ways: first, the frequency with which observed concentrations exceeded objectives or guidelines was tabulated, and, second, the degree to which observed concentrations exceeded objectives or guidelines was calculated. The degree of exceedance is presented as a "mean exceedance ratio". For chemical parameters, this was calculated as the arithmetic mean ratio of observed concentrations to the given objective or guideline. For fecal coliform bacteria the water quality objective is based on a geometric mean of samples collected. Therefore, the mean exceedance ratio for fecal coliforms was calculated as the ratio of the observed geometric mean fecal coliform count to the objective.

Fecal Coliforms (100 counts/100 ml; MOE 1984)

In general, EC counts were almost always over 90% of FC counts. Seventy-five percent and 87% of the FC values exceeded the objective for Dry Events 1 and 2 respectively. In contrast, during Dry Event 3 only 28% of the FC values exceeded the objective. For both the Wet Event and the wet portion of Dry Event 2, 98% of the FC values exceeded the objective.

In general, wet weather mean exceedance ratios were greater than dry weather mean exceedance ratios. Wet Event mean exceedance ratios were greater on the West Humber and East Humber Rivers than on the Humber River.

Fecal coliform levels immediately downstream of the towns of Woodbridge and Bolton (i.e. stations H-18, E-8 and H-9) were consistently higher than the FC levels of stations located just upstream from these communities.

Extremely high FC counts regularly occurred at stations H-2 and W-2.

In general FC:FS mean ratios were less than 4 during all events throughout the Humber watershed. Ratios greater than 4 consistently occurred at W-6 and W-5(T) in Dry Event 1 and at E-2 and H-2 in Dry Event 3. Ratios less than 0.5 consistently occurred at H-55(T) in Dry Event 1, at H-20 in Dry Event 2 and at E-9 and H-8 in Dry Event 3.

Pseudomonas aeruginosa (PA)

In general, PA counts tended to increase in subbasins with urban inputs. Dry and wet weather counts generally were greater than 10 below Bolton in the Humber, and in the East Humber upstream of E-4. However, PA counts in the West Humber were also high in the Wet Event. PA counts in Dry Event 3 were all generally less than 5.

Total Suspended Solids (25 mg/l; McNeely et al. 1979)

The TSS guideline was exceeded by 24%, 16% and 5% of the samples for Dry Events 1, 2 and 3 respectively. Exceedances occurred only in the lower portion of the watershed, and were limited to seven stations in Dry Event 1 (H-17, H-15, H-14 H-11 H-9, E-7(T), W-6), three stations in Dry Event 2 (H-17, H-15, H-14), and two stations in Dry Event 3 (H-15, H-14). Dry weather mean exceedance ratios were low.

Sixty-eight percent of samples collected during the wet portion of Dry Event 2 exceeded the guideline, as did 84% of samples collected during the Wet Event. With the exception of station H-55(T), wet weather exceedances occurred at all stations. Station H-55(T) was located immediately downstream of the

swimming pond in Albion Hills Conservation Area; suspended particles likely settle in the pond before reaching the sampling station. Mean exceedance ratios for the wet portion of Dry Event 2 were generally greater than those recorded for the Wet Event; the greatest exceedances occurred in the lower stretches of the Humber River.

Total Phosphorus (0.03 mg/l; MOE 1984)

The percentage of samples which exceeded the TP guideline was 91% in Dry Event 1, 47% in Dry Event 2, and 19% in Dry Event 3. Ninety-seven percent and 94% of samples exceeded the guideline for the wet portion of Dry Event 2 and the Wet Event, respectively.

Dry weather mean exceedance ratios were uniformly low throughout the study area. As noted for TSS, TP mean exceedance ratios for the wet portion of Dry Event 2 were highest in the lower stretches of the Humber River and were generally greater than the TP mean exceedance ratios of the Wet Event.

Copper (0.005 mg/l; MOE 1984)

The Cu objective was exceeded in 98% and 82% of the samples for Dry Events 1 and 2 respectively. In contrast, no exceedances were recorded for Dry Event 3. During wet weather sampling the objective was exceeded in 92% and 88% of the samples for the wet portion of Dry Event 2 and the Wet Event respectively.

For all events except Dry Event 3, mean exceedance ratios were greater than one at all sampling stations. Generally these mean exceedance ratios were similar for both dry and wet weather samples, although some of the mean exceedance ratios during wet

conditions were actually lower than those recorded for Dry events 1 and 2. This may indicate that dry weather sources of Cu were diluted in wet conditions.

Lead (0.025 mg/l; MOE 1984)

The Pb objective was never exceeded during Dry Event 3 and on only one occasion during Dry Event 1. In contrast, exceedances occurred in 71% of the samples during Dry Event 2; all stations except H-15 had at least one exceedance. Lower base flows during Dry Event 2 may have reduced the watershed's capacity to dilute Pb inputs resulting in higher Pb concentrations during this event.

Mean exceedance ratios were uniformly low throughout the watershed.

Parameter Correlations

Spearman rank correlation coefficients were calculated on the combined dry weather chemical data, and also on the event chemical data.

In dry weather, TDS and COND were positively correlated with Q and negatively correlated with TSS and Pb. Positive correlations occurred frequently between TSS and each of OP, TP, Cu and Pb, between Cu and each of OP, TP, and Pb, and between TP and OP.

Some changes in parameter correlations occurred in the Wet Event. Total suspended solids, OP, and TP became positively correlated with Q; OP, TP, and Cd exhibited more frequent correlations with TSS, whereas Cu and Pb correlations with TSS were less frequent. Copper and Pb were no longer negatively correlated with Q. Cadmium became positively correlated with Cu and Pb.

Description of Wet Event

For the purposes of the study, the Wet Event period encompassed six days, from November 9 to 14, 1984. The event was considered to run from 12:00 AM, Friday November 9 (0 hours) to 12:00 AM, Thursday November 15 (144 hours). To avoid possible confusion when comparing hydrographs or pollutographs from various stations, this six-day period will be hereafter referred to in terms of total event time (0 to 144 hours).

A total of 35mm of rain fell between the afternoon of November 9 and the early evening of November 11. The major portion of the event occurred between 42 and 66 hours (November 10 and 11), when 22 mm of rain fell. These heavy rains were preceded by three intense rainfalls of short duration.

A typical hydrograph is presented in Figure 2. On the figure, the period of rainfall in the study area, the flow event, and the sampled portion of the flow event is shown. The "flow event" was defined as the interval from the first rise in the hydrograph at that station until a return to near base flow when the final chemical samples were taken. The period of sampling indicated refers to chemical and microbiological sampling; not included are additional microbiological samples which were collected on November 14.

It can be seen from Figure 2 that, based on discharge, a significant percentage of the flow event was sampled. As previously mentioned, Wet Event chemical loads were defined as the total chemical mass that flowed out of a subbasin during the sampled portion of the event. Caution must be exercised in making comparisons of chemical loadings between stations because some spurious differences may occur if the portion of the flow event sampled was not exactly the same at each station. The hydrograph shown is more or less typical of all the sampling

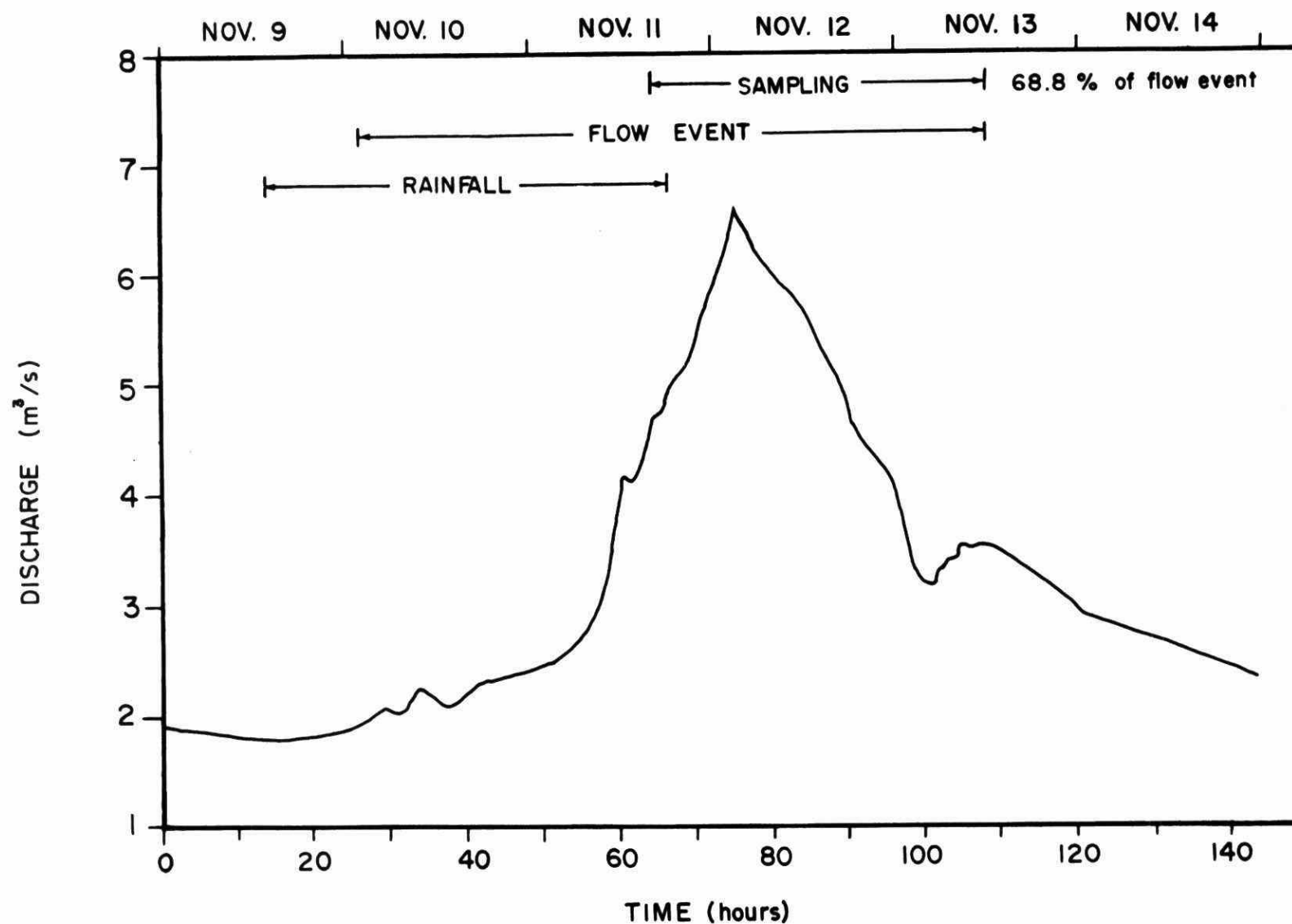
stations in that the peaks and falling portions of the hydrographs were sampled.

"Pollutographs", plots of chemical concentrations versus time, were plotted for stations at the confluence of each of the 3 tributaries. At station E-8 the concentrations of TSS, TP, Cu, Pb and Cd all closely paralleled discharge. At station H-14 parameter concentrations also paralleled discharge, although Cd and Cu concentrations increased again approximately 15 hours after the hydrographic peak. Compared to stations H-14 and E-8, obvious differences occurred in the temporal pattern of contaminant inputs at station W-6. At this station the peak concentrations of TSS TP Cu Pb and Cd all preceded the hydrographic peak by at least 10 hours. This suggests that, in terms of contaminant inputs at station W-6, the initial runoff period is of greatest significance.

It is interesting to note the close association of TSS and TP in all of the examples. The implication is that phosphorus is largely sediment-transported. A similar association may exist between TSS and metals, however, the pollutographs indicate that some departures from this occur.

Subbasin Chemical Loadings

For each event the mean chemical contributions (i.e. discharge (Q), TSS, TP, Cu, Pb, Cd) of the subbasins were displayed on schematic diagrams of the Upper Humber watershed. Subbasin chemical contributions were represented as percentages of the loadings at the "mouth" of the Upper Humber watershed, the "mouth" being defined as the southern-most boundary of the study area. As the confluence of the West Humber River with the Humber River is downstream of the study area boundary (Figure 1) it was necessary to consider the West Humber separately from the Humber



- 312 -

and East Humber Rivers. Therefore, subbasin chemical loadings were expressed as a percentage of the loading at Highway 7 (station W-6) for the West Humber River stations, and as a percentage of the loading at Steeles Avenue (station H-17) for all other stations. Obviously it was possible in some instances for the subbasin loadings of certain parameters to exceed those occurring at the "mouth". In those cases the subbasin loading percentages were recorded as values greater than 100%.

Chemical loadings by subbasin are presented in Figures 3 to 7 and Tables 1 to 5 and are discussed below.

Total Suspended Solids

Dry weather TSS contributions were minimal from the Humber River upstream of the Albion Hills. Although subbasin H-6 accounted for just over 50% of the Upper Humber River's dry weather discharge, it contributed less than 15% of the TSS load. Similarly, the tributaries "Coffey Creek" (H-4(T)), Centreville Creek (H-55(T)), and Cold Creek (H-10(T)) contributed little to the total TSS load. In Dry Events 1 and 2 there was an increase in TSS loading through the town of Bolton, although this trend was reversed in Dry Event 3. The greatest dry weather contributions of TSS occurred downstream of Bolton within subbasins H-11, H-14, and especially H-15. The East Humber River acted as relatively clean dilution for the Humber River at Woodbridge.

Relative to the Humber River, the West Humber River's dry weather discharge is minimal ($\leq 10\%$ of the Humber River's discharge); the river becomes intermittent in summer. The West Humber River upstream of subbasin W-15 contributed virtually nothing to the system in dry weather. In terms of TSS, "Gore Creek" (subbasins W-5(T) and W-10(T)) likewise contributed minimally in dry weather.

Relative subbasin contributions of the Humber River did not change appreciably during the wet portion of Dry Event 2. On the West Humber River, however, there was a marked increase in the relative TSS loading of subbasin W-5(T).

During the Wet Event there was an increase in the relative TSS contribution from the H-6 subbasin. Again there was an increase in TSS load through the town of Bolton, however the relative contributions of subbasins H-11, H-14, and H-15 were lower than in dry weather. In general, the Humber River upstream of Woodbridge accounted for a smaller proportion of the total discharge than it had in dry weather - only 50% in the wet event compared with 70 to 80% in dry weather. The relative contribution of the East Humber River to total discharge was also reduced. This indicates the increased importance of subbasin H-17 in the Wet Event. This trend was not evident in the wet portion of Dry Event 2, suggesting that there may be differences in the way the watershed responds to various storm events.

On the West Humber River, the major TSS inputs during the Wet Event occurred within the W-6 subbasin; as in dry weather, the other subbasins contributed relatively little to the total TSS load. In the Wet Event, the discharge of the West Humber River relative to the Humber River increased to 33%. Relative impacts of the two rivers on the lower Humber are hard to determine based on our data because the West Humber River passes through Claireville Reservoir between station W-6 and its confluence with the Humber River near Weston Road.

Total Phosphorus

Total phosphorus contributions varied considerably between Dry Events 1, 2 and 3. Exceptions were the relative loadings from the upstream Humber River tributaries H-4(T), H-55(T) and

Table 1: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 1.

Station	Parameter									
	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	TSS Loading (mg/s)	Conc. (mg/l)	TP Loading (mg/s)	Conc. (mg/l)	Cu Loading (mg/s)	Conc. (mg/l)	Pb Loading (mg/s)	Conc. (mg/l)
H-17	540	1.41	36067	25.58	84.8	0.060	15.1	0.011	26.4	0.019
H-15	290	1.07	43229	40.40	70.8	0.066	12.6	0.012	19.3	0.018
H-14	281	1.12	27000	24.11	64	0.057	21	0.019	21	0.019
H-11	268	1.13	30977	27.41	60.5	0.054	13.2	0.012	20.7	0.018
H-10(T)	63	0.24	1927	8.03	14.4	0.060	3.04	0.013	4.09	0.017
H-9	188	0.88	22168	25.19	58.8	0.067	13	0.015	14.2	0.016
H-75	177	0.77	7556	9.81	34.2	0.044	13.7	0.018	13.5	0.018
H-6	146	0.85	4278	5.03	42.8	0.050	21.2	0.025	14.6	0.017
H-55(T)	44	0.16	1264	7.90	8.26	0.052	2.24	0.014	2.58	0.016
H-4(T)	23	0.16	827	5.17	6.59	0.041	2.24	0.014	2.72	0.017
E-8	194	0.56	2992	5.34	26.2	0.047	9.33	0.017	11.3	0.020
E-7(T)	35	0.077	2549	33.10	4.64	0.060	0.87	0.011	1.68	0.022
E-6	141	0.14	2833	20.24	10.4	0.074	0.9	0.006	2.63	0.019
E-4	95	0.18	3721	20.67	12.4	0.069	2.18	0.012	3.81	0.021
W-6	143	0.088	2460	27.95	5.9	0.067	1.78	0.020	1.65	0.019
W-5(T)	59	0.02	108	5.40	1.52	0.076	0.29	0.015	0.35	0.018
W-10(T)	21	0.028	119	4.25	1.85	0.066	0.41	0.015	0.5	0.018
W-15	32	0.0037	10	2.70	0.073	0.020	0.069	0.019	0.056	0.015

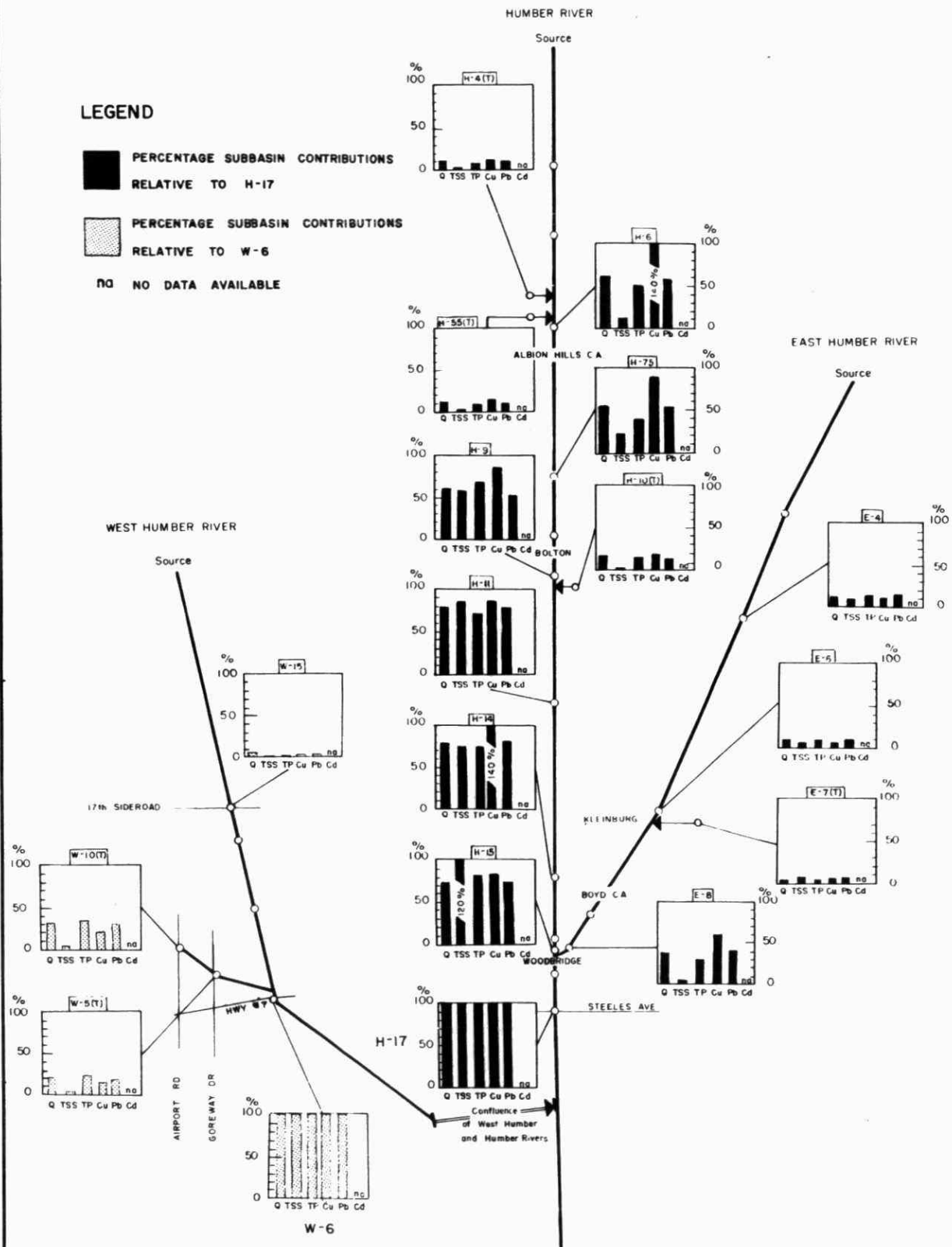


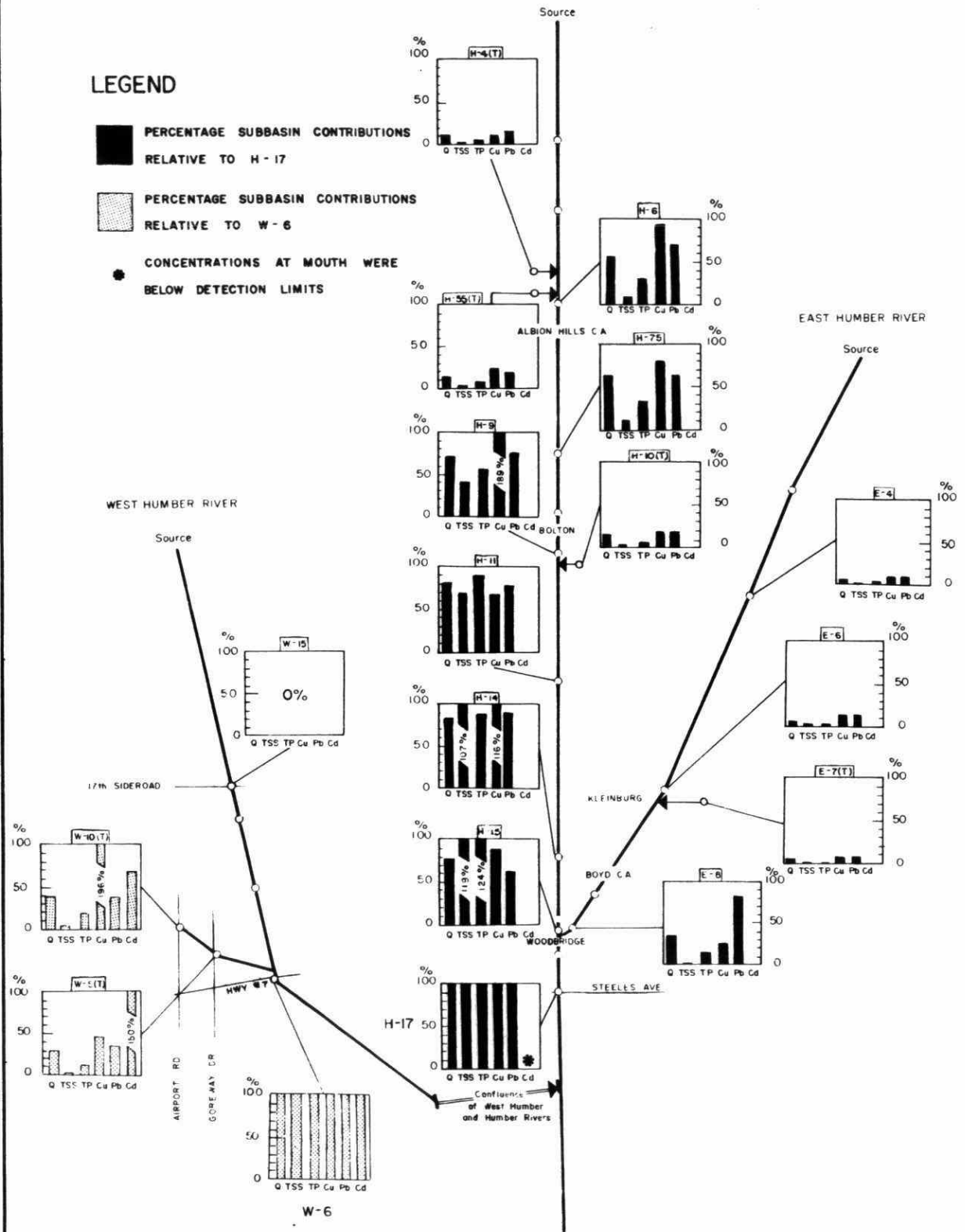
Table 2: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 2.

Station	Parameter									
	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	TSS Loading (mg/s)	Conc. (mg/l)	TP Loading (mg/s)	Conc. (mg/l)	Cu Loading (mg/s)	Conc. (mg/l)	Pb Loading (mg/s)	Conc. (mg/l)
H-17	540	1.22	34800	28.52	66.6	0.055	9.47	0.008	29.4	0.024
H-15	290	0.97	41299	42.58	82.4	0.085	8.31	0.009	18.5	0.019
H-14	281	1.01	37100	36.73	59	0.058	11	0.011	26	0.026
H-11	268	0.98	23628	24.11	59.2	0.060	6.63	0.007	22.7	0.023
H-10(T)	63	0.22	1220	5.55	4.63	0.021	1.82	0.008	5.64	0.026
H-9	188	0.85	14091	16.58	38.8	0.046	18.6	0.022	22.2	0.026
H-75	177	0.77	4252	5.52	23.6	0.031	7.73	0.010	18.6	0.024
H-6	146	0.69	3105	4.50	20	0.029	9.14	0.013	21.4	0.031
H-55(T)	44	0.17	1276	7.51	5.85	0.034	2.29	0.013	5.8	0.034
H-4(T)	23	0.13	976	7.51	3.84	0.030	1.14	0.009	4.57	0.035
E-8	194	0.46	2295	4.99	9.78	0.021	2.63	0.006	23.7	0.052
E-7(T)	35	0.073	584	8.00	1.02	0.014	0.74	0.010	3.14	0.043
E-6	141	0.33	1102	3.34	2.45	0.007	1.21	0.004	3.66	0.011
E-4	95	0.073	292	4.00	1.63	0.022	0.83	0.011	2.71	0.037
W-6	143	0.08	1680	21.00	4.16	0.052	0.56	0.007	2.64	0.033
W-5(T)	59	0.024	23	0.96	0.41	0.017	0.26	0.011	0.92	0.038
W-10(T)	21	0.03	103	3.43	0.83	0.028	1.1	0.037	1.03	0.034
W-15	32	0	0	0.00	0	0.000	0	0.000	0	0.000

HUMBER RIVER

LEGEND

- PERCENTAGE SUBBASIN CONTRIBUTIONS
RELATIVE TO H-17
- PERCENTAGE SUBBASIN CONTRIBUTIONS
RELATIVE TO W-6
- CONCENTRATIONS AT MOUTH WERE
BELOW DETECTION LIMITS



the metropolitan toronto and region
conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

CHEMICAL LOADINGS BY SUBBASIN
DRY EVENT 2 (DRY PORTION)

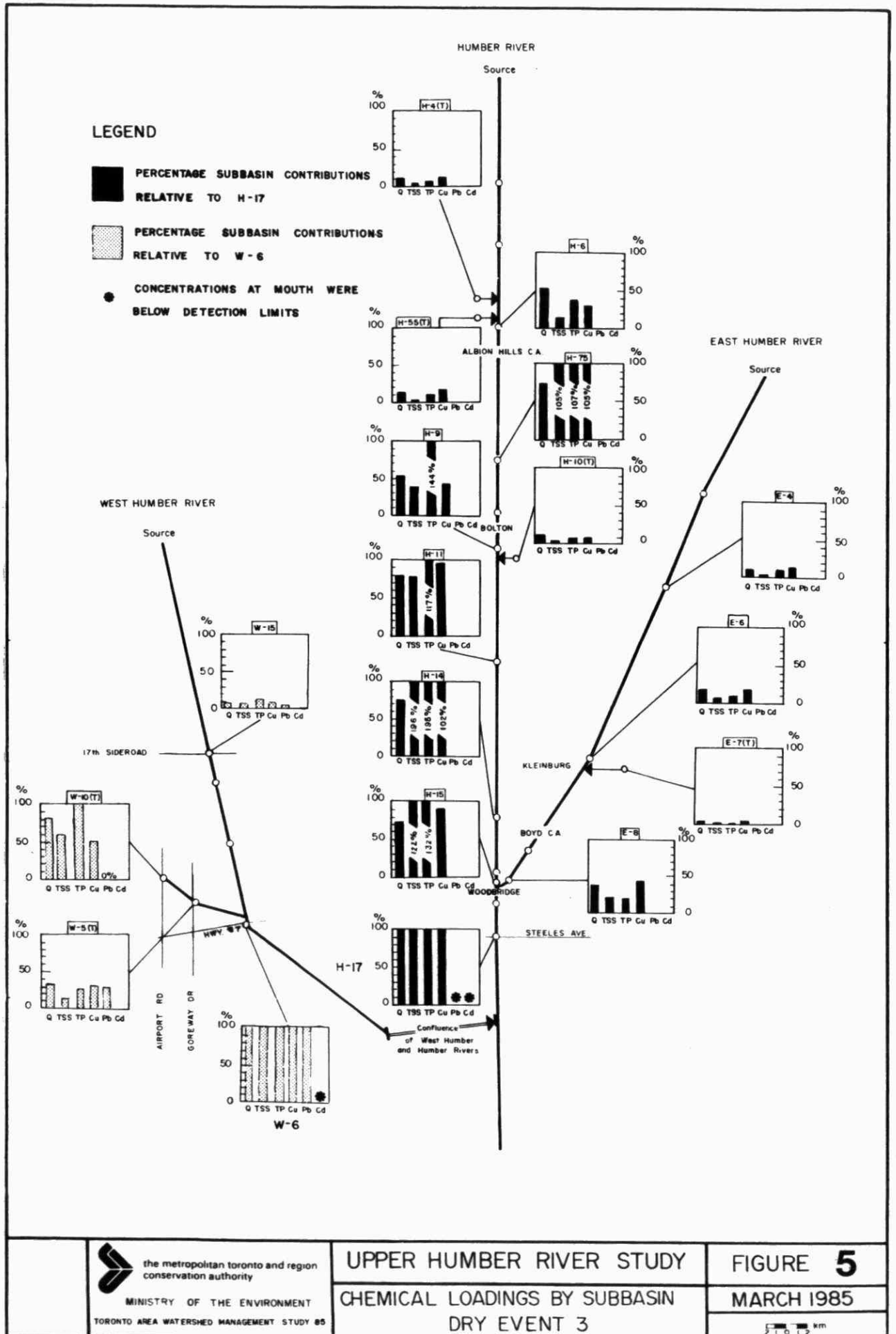
FIGURE 4

MARCH 1985

0 1 2 km

Table 3: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 3.

Station	Parameter									
	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	TSS Loading (mg/s)	Conc. (mg/l)	TP Loading (mg/s)	Conc. (mg/l)	Cu Loading (mg/s)	Conc. (mg/l)	Pb Loading (mg/s)	Conc. (mg/l)
H-17	540	2.36	23512	9.96	40.9	0.017	3.95	0.002	0	0.000
H-15	290	1.76	28676	16.29	54.2	0.031	3.59	0.002	0	0.000
H-14	281	1.76	46100	26.19	80	0.045	4	0.002	0	0.000
H-11	268	1.88	18591	9.89	47.6	0.025	3.77	0.002	0	0.000
H-10(T)	63	0.3	1082	3.61	3.43	0.011	0.3	0.001	0	0.000
H-9	188	1.24	9014	7.27	59.4	0.048	1.63	0.001	0	0.000
H-75	177	1.78	24738	13.90	43.8	0.025	4.14	0.002	0	0.000
H-6	146	1.25	3030	2.42	16.3	0.013	1.25	0.001	0	0.000
H-55(T)	44	0.3	757	2.52	4.09	0.014	0.6	0.002	0	0.000
H-4(T)	23	0.27	730	2.70	2.87	0.011	0.45	0.002	0	0.000
E-8	194	0.92	4723	5.13	8.26	0.009	1.84	0.002	0	0.000
E-7(T)	35	0.1	482	4.82	0.52	0.005	0.17	0.002	0	0.000
E-6	141	0.43	1818	4.23	4.13	0.010	0.73	0.002	0	0.000
E-4	95	0.26	767	2.95	4.16	0.016	0.53	0.002	0	0.000
W-6	143	0.26	1126	4.33	2.64	0.010	0.81	0.003	0.64	0.002
W-5(T)	59	0.09	155	1.72	0.66	0.007	0.27	0.003	0.19	0.002
W-10(T)	21	0.21	659	3.14	2.6	0.012	0.41	0.002	0	0.000
W-15	32	0.022	80.9	3.68	0.33	0.015	0.066	0.003	0.033	0.002



the metropolitan toronto and region
conservation authority
MINISTRY OF THE ENVIRONMENT
TORONTO AREA WATERSHED MANAGEMENT STUDY #5

UPPER HUMBER RIVER STUDY
CHEMICAL LOADINGS BY SUBBASIN
DRY EVENT 3

FIGURE 5
MARCH 1985

Table 4: Mean Instantaneous Loadings and Mean Concentrations - Dry Event 2 (wet portion).

Station	Parameter									
	Cumulative Drainage Area (sq. km)	Discharge (cu. m/s)	TSS Loading (g/s)	Conc. (mg/l)	TP Loading (g/s)	Conc. (mg/l)	Cu Loading (g/s)	Conc. (mg/l)	Pb Loading (g/s)	Conc. (mg/l)
H-17	540	3.62	1574700	435.00	1180	0.326	90	0.025	253	0.070
H-15	290	3.48	1989400	571.67	694	0.199	90	0.026	255	0.073
H-14	281	3.24	1417000	437.35	1560	0.481	74	0.023	220	0.068
H-11	268	2.34	971000	414.96	1200	0.513	69	0.029	195	0.083
H-10(T)	63	0.39	22100	56.67	35	0.090	3.8	0.010	15	0.038
H-9	188	1.91	249000	130.37	274	0.143	23	0.012	78	0.041
H-75	177	1.71	51000	29.82	118	0.069	16	0.009	62	0.036
H-6	146	1.78	61700	34.66	143	0.080	16	0.009	66	0.037
H-55(T)	44	0.44	3390	7.70	36	0.082	5.8	0.013	15	0.034
H-4(T)	23	0.38	39700	104.47	60	0.158	4.4	0.012	15	0.039
E-8	194	1.42	98900	69.65	130	0.092	20	0.014	75	0.053
E-7(T)	35	0.4	200900	502.25	41	0.103	19	0.048	45	0.113
E-6	141	0.33	23700	71.82	17	0.052	3.3	0.010	18	0.055
E-4	95	0.31	18400	59.35	14	0.045	4.3	0.014	18	0.058
W-6	143	0.42	71400	170.00	75	0.179	7.1	0.017	20	0.048
W-5(T)	59	0.15	39600	264.00	38	0.253	5.9	0.039	7.6	0.051
W-10(T)	21	0.18	17900	99.44	28	0.156	3.3	0.018	6.7	0.037
W-15	32	0.018	124	6.89	0.57	0.032	0.34	0.019	0.72	0.040

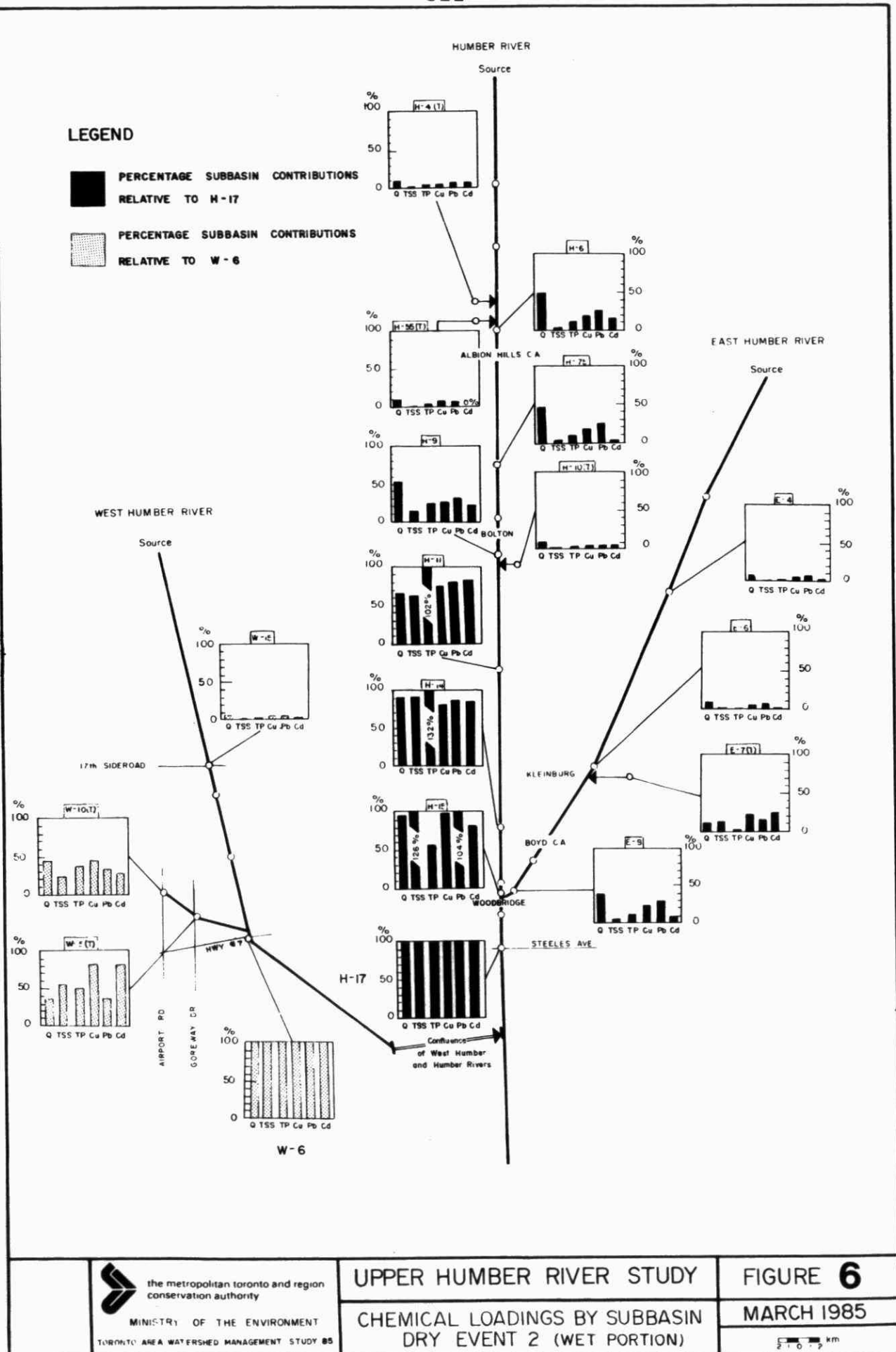
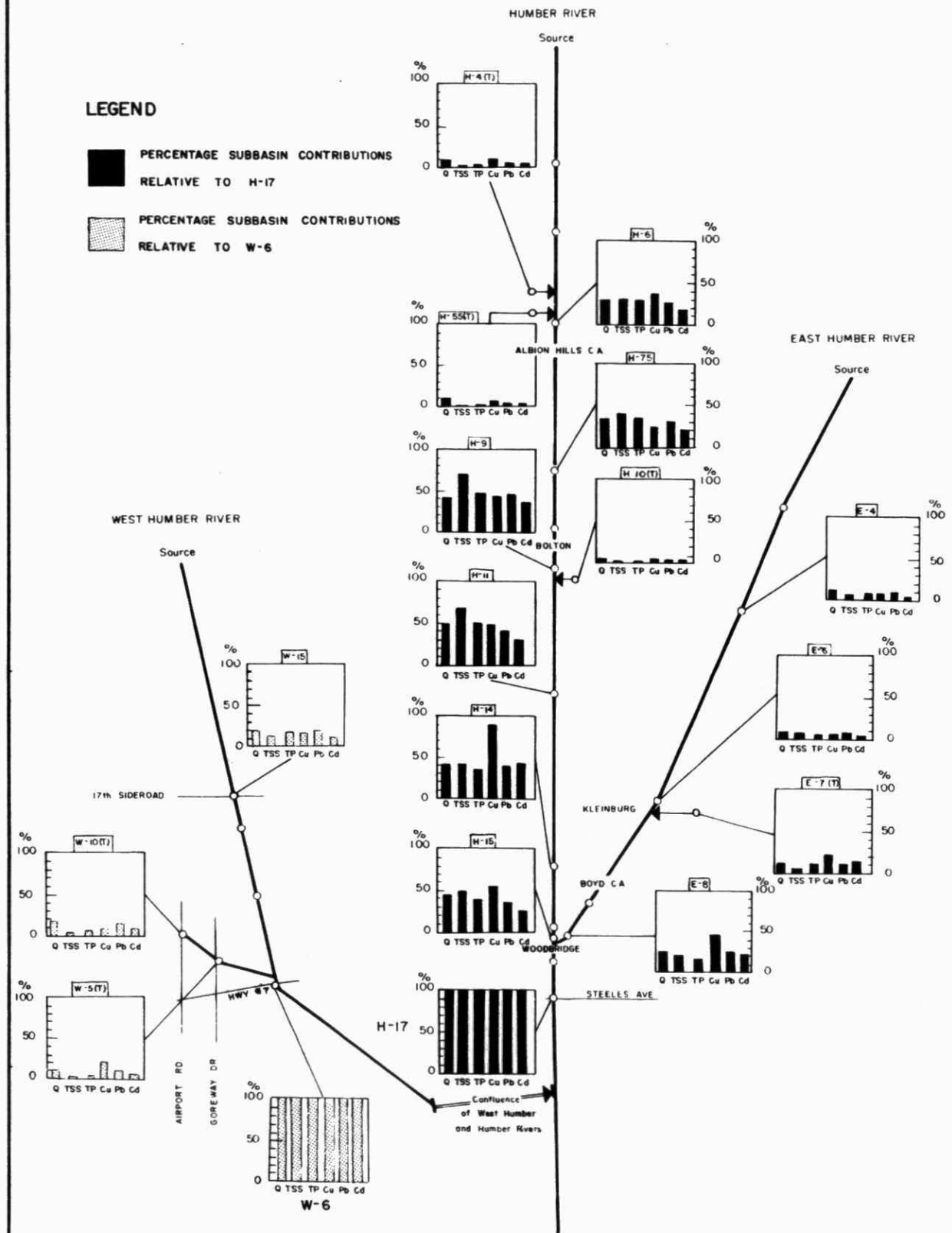


Table 5: Loads and "Mean" Concentrations For Sampled Portion of Wet Event

Station	Parameter									
	Cumulative Drainage Area (sq. km)	Water Volume (x1000 cu.m.)	TSS Loading (kg)	Conc. (mg/l)	TP Loading (kg)	Conc. (mg/l)	Cu Loading (kg)	Conc. (mg/l)	Pb Loading (kg)	Conc. (mg/l)
H-17	540	1872	266379	142.30	436	0.233	18	0.010	59.2	0.032
H-15	290	856	133961	156.50	169	0.197	10.2	0.012	21.8	0.025
H-14	281	770	107135	139.14	157	0.204	16	0.021	22.1	0.029
H-11	268	924	182183	197.17	226	0.245	8.79	0.010	27.3	0.030
H-10(T)	63	99.6	3805	38.20	6.85	0.069	1.56	0.016	2.74	0.028
H-9	188	790	185143	234.36	208	0.263	7.76	0.010	27.7	0.035
H-75	177	688	114160	165.93	150	0.218	4.4	0.006	18.1	0.026
H-6	146	514	87513	170.26	126	0.245	6.52	0.013	16.5	0.032
H-55(T)	44	178	1488	8.36	6.36	0.036	1.35	0.008	3.33	0.019
H-4(T)	23	167	7789	46.64	13.7	0.082	2.18	0.013	3.93	0.024
E-8	194	490	59469	121.37	76.7	0.157	8.76	0.018	14.2	0.029
E-7(T)	35	215	37551	174.66	49.8	0.232	4.3	0.020	6.62	0.031
E-6	141	189	24922	131.86	31.3	0.166	1.32	0.007	5.24	0.028
E-4	95	211	15925	75.47	29.1	0.138	1.3	0.006	5.32	0.025
W-6	143	622	84545	135.92	195	0.314	6.87	0.011	19.4	0.031
W-5(T)	59	67.3	2618	38.90	13.2	0.196	1.49	0.022	1.66	0.025
W-10(T)	21	115	3407	29.63	12.9	0.112	0.73	0.006	2.77	0.024
W-15	32	136	13211	97.14	36.1	0.265	1.2	0.009	3.73	0.027



the metropolitan toronto and region
conservation authority

MINISTRY OF THE ENVIRONMENT

TORONTO AREA WATERSHED MANAGEMENT STUDY 85

UPPER HUMBER RIVER STUDY

CHEMICAL LOADINGS BY SUBBASIN
WET EVENT

FIGURE 7

MARCH 1985

0 1 2 km

H-10(T), which were consistently low. In no dry event did the loadings from any of these subbasins exceed 20% of the loading at H-17. Unlike TSS, TP loadings from subbasin H-6 corresponded closely to stream discharge, approaching 50% of the TP loading at H-17 during Dry Events 1 and 3. Loadings were slightly lower during the second event. Under all dry event conditions, the TP loadings increased between stations H-75 and H-9 (i.e. through the town of Bolton). During each event, the relative loadings increased about 30%; from 35 to 65% of the loading at Steeles Avenue during Dry Events 1 and 2 and from 107 to 144% during Dry Event 3. These loading increases are likely due to the Bolton STP discharge.

During dry weather conditions, relative TP contributions from subbasins through the central and southern portions of the Humber River (i.e. H-11, H-14 and H-15) ranged from 75 to 195% of the levels at H-17. The latter contribution occurred from the H-14 subbasin during Dry Event 3. Comparatively speaking, total phosphorus loadings from these subbasins generally exceeded corresponding stream discharges relative to values at H-17.

Total phosphorus inputs from the East Humber River subbasins were comparatively small relative to the loadings at Steeles Avenue. The most significant contribution occurred from the E-8 subbasin during Dry Event 1, when the TP loading was about 30% of the value at H-17.

Dry weather TP contributions from subbasins on the West Humber River were generally small relative to the loading at W-6. An exception occurred from the W-10(T) subbasin during Dry Event 3, when TP loading was equal to the loading at W-6.

Certain loading trends noted during the Dry Events were also seen during wet weather conditions. For example, the relative TP contributions from the tributary subbasins H-4(T), H-55(T) and

H-10(T) were also minimal during wet weather sampling. Similarly, increases in the relative TP loadings through the town of Bolton were observed during both the wet portion of Dry Event 2 and the Wet Event, although they were not as dramatic as those which occurred during the dry events. Differences in TP loadings from the H-11, H-14 and H-15 subbasins were apparent between the two wet weather sampling periods. Relative to H-17, the more significant contributions from these subbasins occurred during the wet portion of Dry Event 2.

Typically, wet weather TP loadings were relatively small from the East Humber River subbasins. Subbasin contributions were generally less than 10% of the value at H-17, increasing to about 20% at station E-8, near Woodbridge. Relative to station H-17, the discharge contribution from most East Humber River subbasins exceeded the corresponding TP contribution.

On the West Humber River during the wet portion of Dry Event 2, the most significant TP contributions occurred from the W-10(T) and W-5(T) subbasins, with respective loadings of 40 and 50%, relative to the value at W-6. During the Wet Event, relative TP contributions from these subbasins were much smaller.

Copper

In Dry Events 1 and 2, Cu loadings at H-6, the chemical sampling station closest to the source on the Humber River, had already reached the levels of the Humber River at Steeles Avenue. Although this was not the case in Dry Event 3, high loadings were found at the next station downstream, station H-75. The relative Cu contributions of the tributaries H-4(T), H-55(T), and H-10(T) in the three dry events were generally equal to their relative discharge contributions. The same was the case for most of the East Humber River, however, in the E-8 subbasin, relative Cu

loadings tended to exceed relative discharges suggesting that subbasin E-8 could be a Cu source.

On the West Humber River, contributions of subbasin W-15 were minimal. Subbasins W-5(T) and especially W-10(T) had relatively high Cu contributions in Dry Event 2.

In wet weather, the relative Cu contributions from the upper portions of the Humber River were not as high as they had been in dry weather. In the wet portion of Dry Event 2, Cu loadings did not reach the level of Steeles Avenue until subbasin H-11. In the Wet Event, this occurred even further downstream, in subbasin H-14, however, relative loadings then decreased in subbasin H-15. Subbasin E-7(T) had a high Cu contribution in wet weather relative to its discharge. Wet Event Cu loadings at station E-8 reached nearly 50% of the Cu loading at station H-17.

There were high Cu contributions from subbasins W-5(T) and W-10(T) during the wet portion of Dry Event 2, however, this was not the case in the Wet Event. In the Wet Event, the bulk of the West Humber River's Cu load came from subbasin W-6.

Lead

The relative Pb contributions from subbasins throughout the study area were very similar during Dry Events 1 and 2. From almost every subbasin the loadings closely paralleled stream discharge, possibly suggesting inputs were generally of a diffuse nature.

Within the Humber River watershed, loadings from the tributaries H-4(T), H-55(T) and H-10(T) were minimal. Between stations H-6 in the Albion Hills and H-14 in the lower stretches loadings were typically between 60 and 85% of the loading at Steeles Avenue.

On the East Humber River, relative subbasin contributions were generally smaller due to lower stream discharges. An exception occurred from the E-8 subbasin near Woodbridge, where Pb loading was 40% of the value at H-17 during Dry Event 1 and 80% during Dry Event 2. This relative subbasin loading during Dry Event 2 is noteworthy because the corresponding stream discharge was only 40% and, thus, this is the only instance when Pb loading varied appreciably from discharge during either Dry Events 1 or 2.

On the West Humber River, the relative Pb contribution during Dry Events 1 and 2 was minimal from the W-15 subbasin. From subbasins W-10(T) and W-5(T), the respective loadings averaged 35 and 25% of the loading at W-6.

During Dry Event 3, all Pb levels in the Humber and East Humber Rivers were below the detection limit and, therefore, no relative parameter loadings could be determined for these rivers.

On the West Humber River, during Dry Event 3, the relative Pb loading was minimal from subbasin W-15. At W-10(T) the Pb concentration was below detection, despite a comparatively large proportion of stream discharge (80%), relative to W-6. Lead loading from subbasin W-5(T) was about 30% of the value at W-6.

As was the case with Cu loadings, relative Pb contributions from subbasins during wet weather conditions were generally not as high as had been noted during dry weather. This may suggest that dry weather sources of Pb become diluted during wet weather conditions. Relative Pb loadings during the wet portion of Dry Event 2 were similar to those occurring during dry weather conditions in that they generally corresponded to stream discharge. The exceptions occurred in the upper reaches of the Humber River, where the relative Pb contributions from subbasins H-6, H-75 and H-9 were only about 30% of the value at H-17, while the corresponding stream discharges were about 50%.

During the Wet Event, it appeared that a large proportion of the Pb loading was contributed by the H-17 subbasin itself. The relative Pb contribution at station H-15 on the Humber River was only 37% of the value at Steeles Avenue, and at station E-8 on the East Humber River, the relative loading was 24%. Stream discharges were correspondingly low suggesting that during severe storm events the relative contributions from the H-17 subbasin can be significant.

Relative to station W-6, the percentage contributions from the other subbasins on the West Humber River (W-15, W-10(T) and W-5(T)), were lower during the Wet Event than those recorded during Dry Events 1 and 2 (dry and wet portion).

Bed Sediment Chemistry

All but one of the 19 sediment samples collected from stations in the Upper Humber watershed were classified as very fine sand based on grain size analysis. Station W-5(T) was classified as medium to coarse sand. Silts and clays represented less than 3% by weight at all stations.

Cadmium concentrations were less than the detection limit (1.0 mg/kg) at all stations, and were therefore excluded from all subsequent analyses. Basic statistical analyses were performed on the remaining chemical data and the results are as follows:

	<u>Mean</u>	<u>Minimum</u>	<u>Maximum</u>
TP(mg/kg)	245	25 @ H-9	850 @ W-10(T)
Cu(mg/kg)	17	6 @ H-11, E-4	38 @ W-10(T)
Pb(mg/kg)	16	4 @ E-4	48 @ W-10(T)
Zn(mg/kg)	61	30 @ E-4	104 @ E-8

Stations were divided into two arbitrary groups; those with "low" concentrations and those with "high" concentrations as follows:

TP:	> 300 mg/kg	@	H-14, H-9, H-55(T), W-10(T), W-15
	< 100 mg/kg	@	H-17, H-11, E-6, E-4, W-6
Zn:	> 65 mg/kg	@	H-9, H-55(T), E-8, E-2, W-10(T)
	< 35 mg/kg	@	H-11, E-4, W-5(T)
Cu,Pb:	> 20 mg/kg	@	H-17, H-9(Pb only), E-8, E-2, W-10(T)
	< 10 mg/kg	@	H-11, H-75, H-9(Pb only), E-4

With only two exceptions, contaminant levels were not in exceedance of the MOE's open water disposal guidelines (MOE 1976a, 1978). Exceptions occurred at stations E-8 and E-2 where the Zn concentration exceeded the guideline of 100 mg/kg.

Three groups of variables were positively correlated ($p < 0.05$) as follows:

- 1) Zn, Pb, Cu, and silt.
- 2) Zn, TP, and LOI.
- 3) TP, and very fine sand.

In general, these correlations suggest that fluctuations in concentrations of metals and TP parallel fluctuations in the proportion of silt and very fine sand respectively. Also, comparatively high concentrations of Zn and TP are found in sediment of high organic content. Lead and Cu do not exhibit this positive association with organic content.

Land Use

Crop farming (Agriculture) forms the major proportion of land use within the Upper Humber study area. This land use presently comprises 69%, 81% and 87% of the Humber, East Humber and West Humber River basins respectively.

Within the Humber River watershed, pasture land (Pasture) tends to predominate in the more northerly subbasins (i.e. H-20, H-2, H-4(T), H-55(T) and H-6). This is likely because of the extremely hummocky terrain in this region which is better suited for livestock grazing than for crop farming. The shift from predominantly pasture land to agricultural land is dramatic as the Humber River exits the Oak Ridges Moraine and begins to flow over the more gently sloping till plain. From subbasin H-75 south to H-17 the agricultural component within each subbasin is typically between 45 to 75%. The proportion of Forested area within each subbasin is fairly consistent, averaging about 15%. The major Urban land use within the Humber River watershed is limited to subbasins encompassing Bolton and Woodbridge (i.e. H-8, H-9, H-19, H-15 and H-18).

Land use within the East Humber River basin parallels that of the Humber River although no significant pasture land was found. A fairly large urban component is present in the E-2 subbasin, due primarily to the communities of King City and Oak Ridges. The urban land use occurring within subbasin E-8 is associated with the town of Woodbridge.

Agricultural land use within the West Humber River basin is significant. It forms between 45 and 96% of the land use within each of the West Humber River subbasins. Grazing areas on the West Humber River typically border either one or both sides of the watercourse, and the field inventory, revealed many areas of extensive livestock access. The Urban and Forested components are minimal within most West Humber River subbasins.

Overland Sediment Delivery

Soil Loss Mapping indicated that the most significant overland delivery potential exists from subbasins in the central and northern portions of the Humber and East Humber River basins.

Overall, the H-10(T) subbasin (Cold Creek), has the potential to deliver the greatest amount of overland sediment, with 1,210 ha of targeted farmland (Appendix 5). Subbasins H-75 and H-11, situated above and below Bolton respectively, and the two upstream tributary subbasins H-4(T) ("Coffey Creek") and H-55(T) (Centreville Creek) all exhibit between 400 and 500 ha of targeted land.

On the East Humber River, the most significant subbasin is E-6 with a targeted area of 1,021 ha. The subbasins E-2, E-4 and the tributary subbasin, E-7(T) have 399, 554, and 430 ha of targeted land respectively.

The West Humber River basin exhibits considerably less overland sediment delivery potential than either of the Humber or East Humber River watersheds. The greatest potential exists in subbasins W-15, W-5(T) and W-6.

Considered in their entirety, the Humber River basin exhibits the greatest amount of targeted land with 4,203 ha targeted, followed by the East Humber River with 2,500 ha and the West Humber River with 863 ha (Appendix 5). If considered on a per unit area basis (ha of High overland sediment delivery potential/km²), the Humber and East Humber River basins are quite similar exhibiting 12 and 13 ha/km² respectively. The West Humber watershed displays about 6 ha/km².

Field Inventory

Stream Bank Erosion

The total area of exposed erosive stream bank was calculated for each subbasin. These total erosive areas were then divided by

the length of inventoried stream bank within the corresponding subbasin so that an estimate of the erosive area per unit length of stream bank (m^2/km) was obtained.

On the Humber River, subbasins H-19, H-14 and H-11 had the greatest per unit length stream bank erosion with values of 1,362, 961, and 624 m^2/km respectively. The increased TSS loadings observed within these subbasins in dry weather may be at least partially attributable to stream bank erosion. All other Humber River subbasins had erosive areas of less than 400 m^2/km , the lowest, 24 m^2/km , was in the uppermost subbasin, H-20. Erosive area was consistently high on the East Humber River, the highest (792 m^2/km) and lowest (384 m^2/km) values occurring within subbasins E-6 and E-2 respectively. Most of the West Humber subbasins had high erosion, although subbasin W-10(T) was low at 100 m^2/km .

Comparing the three rivers in their entirety, the West Humber River had the greatest erosive area per unit length at 1,486 m^2/km , followed by the East Humber at 1,281 m^2/km and the Humber at 949 m^2/km .

It should be emphasized that, while providing a comparative estimate of the degree of stream bank erosion within subbasins, the results are at best only an indicator of sediment loading potential. Soil type, stream discharge, land use, ground water movement and bank slope may substantially alter actual sediment loading from erosion.

Point Sources

Point source inflows were characterized as to whether they were natural (e.g. tributaries or springs) or anthropogenic (e.g. storm sewers, drainpipes, drainage ditches) and whether they were dry or flowing at the time of the inventory.

Anthropogenic inflows upstream of H-75 were primarily from pastoral, residential or small commercial land uses. The headwaters of Centreville Creek (H-55(T)) are in the community of Caledon East where some storm sewer outfalls exist.

Urban inputs were prevalent in subbasins H-9 and H-18 which corresponded to the towns of Bolton and Woodbridge respectively. These inputs were mainly storm sewers, some of which remained flowing in dry weather. Outfalls from sewage treatment plants (STPs) serving Bolton and Kleinburg were located in subbasins H-9 and H-19 respectively.

Anthropogenic inputs in subbasin E-8 corresponded to that area of Woodbridge located within the East Humber River drainage. A large number of anthropogenic inflows were also found on the East Humber River in subbasins E-2 and E-4. Subbasin E-2 included the communities of King City and Oak Ridges. Subbasin E-4 had a mixture of agricultural and commercial land, with most development concentrated along the Highway 400 corridor.

Anthropogenic inflows in the West Humber system were mostly agricultural in nature.

Livestock Access

For each subbasin, the percentage of watercourse length which was subject to livestock access was calculated from field inventories.

On the Humber River, the greatest amounts of livestock access were found in the more southerly subbasins H-19 and H-11 where, respectively, 66% (3.9 km) and 19% (2.0 km) of the river was subject to livestock access. Livestock access may be a contributing factor to the pronounced stream bank erosion problems in these subbasins. Also, TSS and TP loadings generally

increased within these subbasins. Similar bank erosion problems and loading increases in the adjacent subbasin H-14 cannot be attributed to livestock access, however, as none was found.

On the East Humber River, livestock access was noted only in subbasins upstream of Kleinburg. Access was most prevalent in subbasin E-4 where 27% (2.8 km) of the river was affected.

As noted in the Land Use section, livestock pasturing in the West Humber watershed is significant because of its concentration along the watercourses. Field investigations showed that all subbasins were influenced by livestock: percentage access varied from 7% in subbasin W-2 to 73% in subbasin W-5(T). The extremely high FC counts detected throughout the West Humber watershed in wet weather may be partially attributable to runoff from livestock operations located in close proximity to the watercourses.

The generally low FC levels throughout the Upper Humber watershed in Dry Event 3 may relate in part to seasonal variation in pasturing and other farming practices. In contrast to field observations made in the summer and early fall, livestock would not be pastured in December.

4.0 Discussion

Microbiological sampling indicated widespread water quality degradation throughout the Upper Humber watershed. With the exception of Dry Event 3 when levels were somewhat reduced, FC counts regularly exceeded the PWQO at most sampling stations. Exceedances were most pronounced during wet weather. Generally, wet weather FC exceedances on the West Humber and East Humber Rivers were greater than those on the Humber River.

Fecal pollution in the Upper Humber watershed originates from a combination of rural and urban sources. FC:FS ratios in Dry Event 3 upstream of Bolton and Dry Event 1 on Centreville Creek suggest potential livestock fecal pollution. Animal fecal pollution was also indicated in the East Humber upstream of Woodbridge. Even in the relatively undeveloped upper reaches of the watershed FC exceedances were commonplace. For example, at station H-20, near the source of the Humber River, the geometric mean FC density was 112 counts per 100 ml in dry weather. At station H-2, further downstream, the dry weather geometric mean FC density was 1,106 counts per 100 ml. Field investigations indicated that the high FC levels at H-20 were likely the result of a problem in the immediate vicinity of the sampling station. Dry Event 3 FC:FS ratios indicated potential human sources in this area, while Dry Event 2 data suggest animal sources. This points out that, although an area may be largely undeveloped, significant local problems may still exist.

The towns of Bolton and Woodbridge provide good examples of the effects of local urbanization in the watershed. Within both communities there were numerous point sources, some of which were shown to be potentially significant dry weather sources of fecal pollution. Fecal coliform counts regularly increased through the towns and PA counts were generally high downstream of Bolton. High PA counts, which occurred in the upper reaches of the East Humber also indicate human fecal sources.

During the Synoptic Survey and Dry Event sampling the frequency and degree of TSS and TP exceedances were greatest in the Humber River subbasins between Bolton and Woodbridge. As well, these same subbasins (i.e. H-11, H-14, H-15) contributed the greatest dry weather loadings of TSS. These subbasins likewise had significant loadings of TP, however, large increases in TP loading also occurred upstream within the town of Bolton (i.e. subbasin H-9). Total suspended solids and TP increases between

Bolton and Woodbridge may relate in part to the observed stream bank erosion and livestock access problems in this area. Wet weather TSS and TP exceedances were more widespread. Mean exceedance ratios were higher in wet than in dry weather. The Bolton STP is a probable source of TP and TSS in this area.

In contrast to trends noted for TSS and TP, few significant spatial or weather-related differences in Cu or Pb concentrations were observed. These results corroborate other studies which indicate that significant inputs of Cu and Pb to watercourses can occur from diffuse atmospheric sources (precipitation and dry fallout) (Demayo et al. 1980, Demayo and Taylor 1981). One possible exception to this was subbasin E-8 which may be a source of Cu and Pb. The bed sediment sample from station E-8 had comparatively high concentrations of Cu and Pb as well as the highest observed Zn concentration.

The topography of the southwestern portion of the study area differs noticeably from the remainder of the Upper Humber watershed. The typically low relief and impervious nature of the Peel clays which predominate in the West Humber River basin inhibit rainwater retention, and during intense or prolonged storm events the watershed is extremely "flashy". In contrast to the Humber and East Humber River basins which have substantial base-flow contributions throughout the summer months, the summer base-flow component of the West Humber River is generally minimal. During summer months, as the soil loses its moisture, many watercourses in the watershed become intermittent and rely on periodic storm events to initiate flow. The only appreciable ground water contribution in summer occurred within the W-10(T) subbasin ("Gore Creek"), where several flowing springs were noted during field investigations. As a result of these consistent ground water inputs, "Gore Creek" is exceptional in that it maintains a measurable discharge during dry weather.

The significance of the West Humber's unique drainage basin topography was apparent during event sampling. In summer dry weather, the West Humber River had greatly reduced or intermittent flow; "Gore Creek" contributed a significant portion of the system's discharge. Even following the short-lived, intense rainfall in the wet portion of Dry Event 2 discharge in the West Humber River remained rather low. However, in response to the prolonged rainfall of the Wet Event, flow in the West Humber River became torrential, with peak discharge rivalling that of the Humber River at Woodbridge. During the Wet Event, subbasin W-6 became the major discharge and contaminant contributor.

As with subbasin W-6, the H-17 subbasin took on greater importance in the Wet Event. During the Wet Event, discharge and chemical loadings of the Humber River increased approximately 30% through subbasin H-17. This subbasin exhibited no loading increases of this magnitude in any of the other events, including the wet portion of Dry Event 2. The reason for subbasin H-17's increased importance in the Wet Event stems from a major portion of this subbasin being drained by "Rainbow Creek", a tributary which is confluent with the Humber River just above Steeles Avenue. The "Rainbow Creek" drainage basin is topographically similar to the West Humber River and is also urbanized near its confluence with the Humber River.

Other subbasins are likewise influenced by urbanization. For example, in subbasin E-8, near the mouth of the East Humber River, quicker storm water runoff resulted in rapid rises in river levels during the Wet Event.

The great disparity between dry and wet weather outputs of the West Humber drainage basin becomes significant when attempting to assess the relative impacts of the West Humber, Humber and East Humber Rivers on the lower Humber. Although the effects of

Claireville Reservoir are not fully known, it is apparent that the relative impact of the West Humber River on the Lower Humber would be greater under wet as opposed to dry conditions.

The decreased chemical and microbiological concentrations in Dry Event 3 may indicate that the importance of contaminant sources varies with season. The late fall and winter months are characterized by reduced or absent livestock pasturing, crop tillage and construction, frozen soils and stream banks less susceptible to wind and water erosion, and precipitation which is stored on the land as snow until spring. All of these would combine to reduce contaminant inputs to watercourses during this season.

Seasonal factors must also be considered in evaluating the Soil Loss Mapping. This mapping is designed to provide an indication of the relative potential of overland sources to deliver sediment to watercourses on an annual basis. The results of the mapping for the Upper Humber study area were not substantiated by wet weather sampling, however, this discrepancy is not surprising for several reasons. Of most significance is the fact that, on an annual basis, some 80 to 90% of overland sediment inputs typically occur during a critical 4 to 6 week period in the spring (D. Coleman, G. Wall, personal communication). By failing to adequately sample this period of the year, the relative importance of targeted lands (i.e. areas with a High overland delivery potential) appears to be considerably reduced.

Bed Sediment sampling did not appear to be a good indicator of subbasin chemical contributions, perhaps because samples were coarse.

5.0 Conclusions and Recommendations

Conclusions

1. Exceedances of PWQO (or other environmental standards) for FC, TSS, TP, Cu, Pb and Cd occurred under wet and dry conditions throughout the Upper Humber watershed. The magnitude and frequency of exceedance varied with season, with wet versus dry conditions, with characteristics of the storm events and with seasonal changes in land use activities. Sampling results under dry conditions in December (Dry Event 3) indicated lowest pollutant concentrations and loadings. No PWQO exceedances of Zn occurred in the Synoptic Survey, but Zn bed sediment levels on the East Humber at Woodbridge (E-8) and downstream of King City - Oak Ridges (E-2) exceeded Open Lake Disposal Guidelines (OLDG).
2. Fecal Coliform and TP concentrations showed similar trends throughout the watershed. Although the frequency of exceedance was high under both dry and wet conditions, the magnitude of exceedance was much greater in wet weather. Exceedances were particularly frequent in the lower parts of the watercourses, particularly in the Bolton-Woodbridge area. High PA counts in these areas suggest human fecal pollution. Sampling of point source inputs in this area suggests that urban sources may be partially responsible for these elevated FC and TP concentrations. Instream FC:FS ratios tend to support this conclusion. However, livestock access was extensive between Bolton and Woodbridge and this could also be contributing to higher parameter levels. River FC:FS ratios suggest animal fecal pollution occurred

upstream of Bolton on the Humber River, as well as on Centreville Creek and upstream of Woodbridge on the East Humber.

Extensive areas of livestock access occurred throughout the West Humber and on the East Humber east of Nobleton. The effects of livestock access in these areas may help to explain the FC and TP exceedances in the lower parts of these watercourses.

3. Total suspended solids concentrations in excess of 25 mg/l were rare in dry weather and generally occurred in downstream subbasins. Dry weather loading trends were similar in that they were greatest in the lower subbasins (i.e. south of Bolton H-11, H-14, H-15). Urban development and livestock access problems may be aggravating stream bank and channel erosion throughout these subbasins.

During the Wet Event, the main Humber and its tributaries north of Albion Hills made a relatively greater contribution to TSS loading at Steeles Avenue than during dry events. Tributary subbasins there (H-4(T), H-55(T)) had some of the largest areas of high overland sediment delivery potential. Large increases in Wet Event loadings also occurred through Bolton (H-9) and south of Woodbridge (H-17).

4. Copper concentrations usually exceeded PWQO throughout the watershed except during Dry Event 3. The frequency and magnitude of exceedances were similar in dry and wet conditions suggesting that Cu concentrations in surface waters during summer base-flow situations may be comparable to concentrations in storm event runoff from land surfaces. Diffuse atmospheric inputs are the most probable source.

5. Lead concentrations rarely exceeded PWQO during Dry Events 1 and 3, but during wet weather conditions, Pb concentrations increased slightly and exceedances were more common. However, in Dry Event 2 under low flow conditions widespread Pb exceedances occurred suggesting that the capacity of the watershed to dilute dry weather inputs was reduced. Diffuse atmospheric inputs are the most probable source.
6. Weather-related changes in subbasin flow contributions were significant. The West Humber River was intermittent along most of its length in summer dry conditions, yet discharge at Steeles Avenue during the Wet Event rivalled that of the main Humber at Steeles Avenue. This response may be partially explained by topography and soil type. The combination of poor soil permeability and low relief results in high stream discharges during storm events. Discharges in dry weather remain low because the base-flow component due to groundwater is minimal. Because of these discharge characteristics, the pollutant contribution of the West Humber River downstream of Steeles is likely important only during substantial runoff events. Its influence on the main Humber is unknown because all discharges and pollutant loads are mediated by Claireville Reservoir.

During dry weather, the Humber River discharge at Albion Hills (27% of the drainage basin) represented over 50% of the discharge at Steeles Avenue. The East Humber discharge, at its confluence with the main Humber, represented 30 to 40% of the Humber River discharge at Steeles.

During the Wet Event, discharge contributions changed dramatically. The main Humber between its confluence with the East Humber and Steeles Avenue (H-17)

contributed 30% of the discharge at Steeles although it represents only 10.4% of the watershed area. Rainbow Creek, a tributary entering the Humber within this subbasin and urban areas of Woodbridge may be responsible for the increased discharge contribution. Discharge contributions from the Humber River north of Albion Hills and from the East Humber dropped to about 30% and 22% of total flow, respectively.

7. Tributaries were among the subbasins with the largest area of high overland sediment delivery potential (H-10 (T), H-4(T), H-55(T), E-7(T)). The Humber River near Bolton and the East Humber upstream of Kleinburg also had large areas of high overland sediment delivery potential. In total about 7500 ha of land were targeted comprising 12-13% of the Humber drainage area. Impacts of these areas were not apparent during the Wet Event, however, the greatest impact from these areas is probably during spring runoff.
8. Stream bank erosion was most extensive along the West Humber, the main Humber between Bolton and Woodbridge (H-11, H-14, H-15) and the East Humber between Nobleton and Kleinburg (E-6). Impacts from small urban centres and livestock access may be aggravating bank erosion problems in these areas. The West Humber River had the greatest erosion area per unit length followed by the East Humber, then the main Humber.

Recommendations

1. Water quality problems in the Upper Humber watershed, although not of the magnitude of those occurring in the lower Humber, cannot be discounted in the development of

a water management strategy if PWQO are to be achieved. Note that the implementation of pollution control measures in the predominantly rural Upper Humber watershed and the achievement of at least local compliance with PWQO would be less costly than the initiation of control options for the lower Humber River.

2. It is recommended that the MTRCA coordinate an abatement program with MOE Central Region, the Ontario Ministry of Agriculture and Food, and municipalities beginning with fecal pollution point source inputs and those livestock access problems immediately upstream of the swimming areas in the Claireville and Boyd Conservation Areas. Other sources of fecal pollution in the upper Humber should also be addressed followed by point source inputs of trace metals and phosphorus.
3. More thorough evaluation of the behaviour of non-conservative parameters (i.e. FC, TP) should be conducted in the Upper Humber watershed to determine the potential effects of these parameters on the lower Humber River. This would involve obtaining information on the survival of bacteria and time of travel in the watercourses. A review of the microbiological data on the upper Humber should be undertaken in light of recent studies on use of different parameters as indicators of fecal pollution sources.
4. In view of the close association between TSS and contaminants, the role of sediment in pollutant transport should be further investigated. Where trace metals are of interest, sampling suspended as oppose to bed sediment may prove more beneficial.

5. The present and potential impacts of Claireville Reservoir on downstream quality should be evaluated.
6. Seasonal trends in contaminants loadings of the Upper Humber watershed should be further investigated, particularly spring runoff.
7. The relative importance of stream bank erosion and livestock access to instream water quality needs to be further evaluated, especially in the area between Bolton and Woodbridge.
8. A study should be conducted to assess the impacts of ongoing and future land use changes within the Upper Humber watershed.
9. Pathways (e.g. dry atmospheric fallout, precipitation, ground water) by which Cu and Pb enter the Upper Humber system should be further investigated.
10. The MTRCA should continue to apply the Soil Loss Mapping technique to other agricultural lands in its jurisdiction and verify and evaluate the results provided by this methodology.

6.0 Literature Cited

- Baun, K. 1982. Alternative methods of estimating pollutant loads in flowing water. Wisconsin Dept. of Natural Resources. Technical Bulletin No. 133. 11 pp.
- Coleman, D.E. 1982. Identification of priority management areas in the Avon River watershed. Stratford-Avon River Environmental Management Project. Technical Report R-4. 71 pp.
- Demayo, A., M.C. Taylor and S.W. Reeder. 1980. Guidelines for surface water quality. Vol. 1 Inorganic chemical substances. Lead. Environment Canada, Inland Waters Directorate, Water Quality Branch. 36 pp.
- Demayo, A., and M.C. Taylor. 1981. Guidelines for surface water quality. Vol. 1 Inorganic chemical substances. Copper. Environment Canada, Inland Waters Directorate, Water Quality Branch. 55 pp.
- Geldreich, E.E., and B.A. Kenner. 1969. Concepts of fecal streptococci in stream pollution. J. Water Pollut. Contr. Fed. 41: R336-R352.
- King, C.A.M. 1972. Beaches and coasts. 2 ed. Edward Arnold Ltd., London. 570 pp.
- McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Water Quality sourcebook. A guide to water quality parameters. Environment Canada, Inland Waters Directorate, Water Quality Branch. 89 pp.
- MOE 1976a. Evaluating the impact of marine construction activities on water resources.

**Bacteriological Water Quality Study Examining the Impact
of Sediment and Survival Times in the Humber River
and Black Creek**

by

Patricia Seyfried and Elizabeth Harris
Department of Microbiology,
Faculty of Medicine,
University of Toronto.
Toronto, Ontario, M5S 1A8,
Canada

Abstract

Studies to assess the effect of sediment resuspension upon bacterial loading of the water column were carried out at six sites along the upper and lower Humber River and Black Creek. Bacterial contribution from sediment was measured during dry weather (before and after mechanical agitation of the sediment); wet weather; and intermediate periods within two days after a rainfall. The results showed that during dry weather, at locations with consistently high point source bacterial loadings, samples taken from the water column after mechanical sediment agitation exhibited higher fecal coliform and Escherichia coli counts than samples taken before agitation. During wet weather, bacterial densities were usually observed to be higher than those induced by dry weather sediment agitation. This suggests that localized sediment resuspension is only one of a number of sources of bacterial pollution during storm events.

The survival rates of water quality indicator bacteria were also monitored to determine their response to the Humber River environment. Bacterial survival was found to be somewhat

influenced by site-specific factors such as temperature and nutrient input. For example, E. coli exhibited a 80 to 98% die-off rate within 24 hours at sites impacted upon by sewers, while a greater than 99% die-off rate was noted at sites not receiving nutrient enriched effluents. Streptococcus faecalis exhibited die-off rates similar to E. coli at most of the sites, whereas S. faecium survived somewhat longer. All three indicators survived better when the water temperature was lower than 10°C. Streptococcus bovis was found to exhibit rapid die-off in surface waters, i.e. greater than 99% in 24 hours.

Introduction

The impact of fecal pollution upon surface water is dependent upon the type of input and the instream processes that may affect the downstream water quality. Two such processes which may contribute to downstream contamination from point and non-point pollution sources are bacterial transfer between the water column and sediment, and bacterial survival.

Although some bacteria remain free-floating in the aquatic environment, a large number become associated with solid particles (1). The mechanism of bacterial attachment to solid surfaces is by adsorption (2,3). By means of attraction forces, such as Van der Waal and chemical bonding, free-floating bacteria and bacteria-particle aggregates are continually removed from the water column to form part of the bed sediment (4).

Previous studies of the bacterial populations in sediments have shown that bacterial concentrations are considerably higher in the sediment than in the overlying water column (5-8). The bulk of bacteria in sediments reside in the surface layers where their activity is important to the mineralization of organic matter (9, 10). Fecal coliform and enteric pathogenic bacteria, such as Salmonella spp. have also been recovered from the upper two inches of the sediment bed (5, 11). Researchers have shown that higher recoveries of fecal coliform bacteria (100 to 1,000 fold increases over water column levels) may be obtained from sediments and have suggested that sediments may serve as a more concentrated and stable index of water quality (6).

Survival of fecal indicator bacteria in sediments is an important criterion in determining the extent to which they may be found in this environment. Extended survival and even multiplication of fecal coliforms in sediments have been shown to occur (7,8). Such phenomena may be due to the higher levels of organic carbon, ammonium, organic nitrogen and phosphorus found in sediment (12, 13).

Characteristics of the fecal indicator bacteria such as their ability to metabolize benthic nutrients (7, 8), withstand predatory pressure (14, 15), and metabolically compete with other microbes (8, 15) will dictate their survival time in sediments. The rate of sedimentation will also affect the recovery of these bacteria from sediment beds. Sedimentation rates will depend upon the adsorption capacity of both the sediment and the

bacteria. Adsorbance is dictated most specifically by the surface chemistry of the microbe (16). The concentration of bacteria present at the water - solid interphase will also affect the extent of adsorption leading to possible saturation of the sediment surface (17). Inorganic particles in sediments are classified according to size into coarse sands (200 - 2000 μm diameter), fine sands (20 - 200 μm D.), silts (2 - 20 μm D.) and clays (< 2 μm D.). Clays can have a surface area in excess of 20,000 $\text{cm}^2 \text{g}^{-1}$ and thus make the best adsorbents (4). Clays also have an added benefit in that they provide protection from radiation and predator - prey interactions (4).

Some environmental factors affect the rate of sedimentation because they affect the ability of the bacteria to adsorb to sediment particles. A pH >6 will interfere with adsorbance, while the presence of electrolytes and increased salinity will enhance flocculation and sedimentation. Decreasing the salinity will cause desorption of bacteria from sediments (18).

Depth of the water column affects the rate of sedimentation; shallow systems may display an increased sedimentation rate. Sediment resuspension in shallow lakes and other surface waters may occur due to increased discharge rates, waves, and other wind induced turbulence, motor boats, swimming and wading (19). A number of reports have shown sediments to be reservoirs of enteric bacteria in densities sufficient to cause water quality deterioration and possr potential health hazards (20).

Streams and other watersheds represent a more dynamic system for studying the effects of sediment resuspension than lotic waters. Watersheds may be viewed as multiple storage and release systems (21) where water and sediment bacterial populations are in a constant state of interchange i.e. bacterial content in the water column is increased by fecal pollution input and sediment resuspension is reduced by sedimentation and die-off. Sediment resuspension and deposition are stream-flow dependent processes whereby increased flow facilitates the former and decreased flow the latter. How far bacteria are transported during high flow conditions depends upon the stream flow velocity. In a study by Matson et al (19) regression equations of the percent decrease in fecal indicator densities in water between two stations located 2.7 Km apart showed that minimal decrease occurred at high stream velocity (discharge). Since no additional inputs occurred along this portion of the river, the authors concluded that bacteria from upstream inputs were being transported downstream and that no sedimentation was occurring because of the high flow.

In general, water represents a more harsh environment for bacteria than sediments. The levels of available nutrients will be lower than those found in sediments and will vary depending upon the type of pollution input. Where nutrient levels are low, die-off may proceed more rapidly. Water with high dissolved organic carbon content, eg. impacted upon by sewage effluent, may permit extended survival or even support re-growth of heterotrophic bacteria (22). The presence of toxic materials, sunlight,

and changes in water pH will affect the survivability of some types of bacteria (23, 24, 25). Temperature is also known to affect bacterial survival (26). Higher water temperatures will generally cause increased bacterial metabolism and thus an increased rate of decay while low temperatures tend to retard metabolism and permit extended survival by allowing the bacteria to exist in a dormant state. McFeters et al (27) found that E. coli survival response to temperature was inversely proportional between 5 to 15°C, but that above 15°C temperature became a less important factor in survival. Thermal stress can be beneficial to certain bacterial species depending upon their ambient growth temperatures. Regrowth of Pseudomonas aeruginosa in polluted waters at high temperatures can occur, especially when coupled with a high organic content. Some fecal coliform bacteria, eg. Klebsiella sp., will also exhibit regrowth under these conditions.

This study was designed with the following objectives in mind: firstly, to determine the extent of bacterial exchange between sediments and the water column when sediments are resuspended and transported; secondly, to determine the survival time of various fecal indicator bacteria in the Humber River and Black Creek environment; thirdly, to provide the data required to help establish a method of inferring sources, eg. human versus non-human, by identifying the bacteria present at survey locations; and finally, to determine how sediments contribute to bacterial pollutant loading, analyze potential bacterial trans-

port by sediments and the deposition capacity of different reaches of the river, relating effects to source type.

Methods

Sampling sites

Six locations were chosen in the upper and lower Humber River and Black Creek to provide study areas affected by different types of pollution.

The six study areas included:

1. Lower Humber River near Elhart Drive (priority storm sewer #254);
2. Black Creek near Hyde Avenue (combined sewer);
3. Lower Humber River at Emery Creek (receives industrial effluent);
4. Lower Humber River at James Gardens (with gull and geese roosting islands);
5. Upper West Humber River at Teston Road (cattle access area); and
6. Upper Humber River at Bolton (Bolton sewage treatment plant).

A geographical map of the locations is shown in Figure 1.

A total of four instream sampling points were chosen at each location in order to delineate the input source. These sites included:

1. 25 to 30 meters upstream from the source;
2. at source (immediately downstream of the pollution input);

3. 25 to 30 meters downstream; and
4. 50 to 60 meters downstream. Effluent samples from the sewer outfalls as well as samples from Emery Creek were also taken.

Only three of the six sampling sites, namely (1) Elhart Drive, (2) Black Creek, and (4) James Gardens will be discussed in this paper. The remainder of the data is included in a report submitted to the Ontario Ministry of the Environment.

Sampling Procedures

1. Dry weather

Sampling was conducted over a three day period and was preceded by a minimum of two dry weather days. A sample, taken mid-point in the water column, was collected from the farthest downstream site in a study area. The river bottom at the site was raked with a garden rake until sediment resuspension was visible and then a second water sample was taken. This procedure was repeated at each site, moving in an upstream direction. The samples were labelled with respect to the site and study area and whether collection was prior to or after sediment agitation. Samples were chilled en route to the lab and analyzed within 24 hrs. after collection.

2. Wet Weather

Sampling was initiated at the beginning of a rain event, or within 24 hrs. after a rainfall, and was continued over a three day period. Rainfall antecedent periods (i.e. 24 to 48 hrs. after a rainfall) were considered to be inter-mediate weather

conditions. The river bottom was not raked during storm events because the sediment resuspension was occurring naturally. Wet weather samples were collected and treated as described for dry weather samples.

Effluent samples from the sanitary and storm sewer outfalls were taken directly from the pipes. Samples from the combined sewer could only be taken when there was a flow during wet weather.

3. Survival Studies

In situ survival studies of fecal indicator bacteria were conducted at the six study areas in the summer and again in late October and mid-November to assess survival rates under different temperature conditions. Dialysis membrane filter chambers, with volume capacity of approximately 50 or 100 mL, were used to contain the pure cultures of Escherichia coli, Klebsiella pneumoniae, Streptococcus faecalis, S. faecium, or S. bovis. The inoculated chambers were transported to the sites in containers of iced Humber River water. Chambers were submerged and anchored to poles driven in the river bed at the source sampling site. Samples were taken from the chambers on three consecutive days by aseptically removing a small volume of culture and transporting it to the lab on ice. River temperatures were noted during the study.

Bacteriological Analyses

Samples were membrane filtered using Gelman GN6 47 mm cellulose nitrate filters with a pore size of 0.45 μ m.

To assess the number of fecal coliforms, the filters were placed on m-TEC agar and incubated at $44.5^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ for 23 ± 1 hr. Filters with between 10 and 100 target colonies were then removed from the m-TEC plates and placed on filter pads soaked in a urea phenol red solution. A second count of all the urease negative E. coli colonies was then made.

Fecal streptococci were enumerated by planting the filters on m-Enterococcus agar (Difco) and incubating for 48 hrs. at 35°C .

Enterocci were recovered on m-ME agar which also contained indoxyl- β -D-glucoside. The plates were incubated for 48 hrs. at $41.5 \pm 0.5^{\circ}\text{C}$.

Pseudomonas aeruginosa densities were determined using m-PA agar with incubation at 41.5°C for 48 hrs. Data for the two aforementioned parameters are not discussed in this paper.

Analyses of the pure cultures from the survival studies were also performed by membrane filtration using m-TEC for E. coli and K. pneumoniae and m-ENT for the three species of fecal streptococci.

Sediment Size and Weight Analysis

Determination of the suspended sediment weights for both before and after agitation samples was performed by filtration of 100 mL of the sample onto pre-weighed Gelman filters. The filters plus sediment were dried overnight in a 37°C incubator and then weighed to obtain the weight of sediment per 100 mL of water.

Fractional sediment particle sizing was done by filtering 100 mL of the sample through pre-weighed poly-carbonate filters (nucleopore) of progressively smaller pore size. The filters ranging from 12 μm to 0.2 μm , were then dried and weighed to determine the weight of the various size fractions per 100 mL. Samples from selected sites were also submitted for particle size determination using electron microscopy.

Pollution Source Determination

Sources of pollution (i.e. human or non-human) were assessed by the biochemical identification of fecal streptococcal isolates obtained from upstream, source and downstream samples at each site.

Results and Discussion

The Effect of Sediment Resuspension on Water Quality during Different Weather Conditions

Dry Weather

The results showed that in some instances the effect of pollution input was only evident when the bed sediment was agitated (eg. Elhart Drive storm sewer outfall and James Gardens waterfowl access area, Figs. 2 to 7). High upstream levels may have obscured the pollution input; rapid deposition and dilution may also have had an effect. Dilution probably had the greatest influence due to the fact that these two locations are situated on the main Humber River and a comparatively large volume of water passes through each.

At the Black Creek combined sewer outfall (Figs. 8 to 10), a slight increase in the bacterial concentration was seen at the downstream 1 site before mechanical sediment agitation. This could have resulted from the small volume input during dry weather from the combined sewer outfall. Because the creek exhibits approximately 1/10 the flow of the main Humber River, even a small input would be noticeable. The fact that the increase was evident at the downstream site rather than at source was possibly due to the source site location, i.e. too far out in the stream to pick up the small effluent input. This input may not have dispersed through the creek until further downstream. Another factor could have been bacterial desorption from the sandy sediment below the input, since it has been shown that sandy sediments tend to adsorb bacteria more loosely (4).

The overall effect of mechanical sediment resuspension during dry weather was to increase bacterial concentrations in the water column, particularly at the Elhart Drive and James Gardens source sites (Figs. 2 to 7) and at the Black Creek downstream 1 site (Figs. 8 to 10). However, with the exception of the James Gardens source site, the concentrations achieved were not as high as during wet weather, suggesting that local sediment resuspension is only one of many contributing sources during wet weather events. At the James Gardens source site, where fecal coliform and E. coli concentrations were higher during dry weather after mechanical sediment resuspension, it is possible that the wet weather peak was missed since the flow is

swift in this area (average wet weather flow = $4.468 \text{ cm}^3/\text{sec}$. In addition, the sediments at source are composed of very fine organic material which could have been transported downstream at the onset of the storm before sampling had commenced. It is also quite possible that the sediments at this site are so highly contaminated with bird feces that the wet weather contamination from upstream does not have the same impact as resuspension of sediment continuously contaminated with fresh fecal material.

In instances where sediment resuspension brought about little change in the water column fecal indicator levels, such as E. coli levels at Black Creek, the type of pollution input may have been responsible. The combined sewer outfall at Black Creek is a weather dependent input and does not provide constant high level bacterial loadings. Under these conditions fecal indicators such as E. coli, that have a short survival time (i.e. greater than 90% decline in three days) (28), would not exhibit a buildup in the sediments during periods of dry weather. The somewhat greater increases in fecal coliform and fecal streptococcus levels after sediment agitation at the Black Creek upstream and downstream sites is probably due to older inputs since fecal coliforms, other than E. coli and fecal streptococci, tend to survive for longer periods in the environment (29).

Constant dry weather inputs from pollution sources such as the Elhart Drive storm sewer outfall, which exhibits dry weather effluent levels of 25,847 fecal coliforms and 17,692 E. coli per 100 mL, and the James Gardens waterfowl access area provide

continuous bacterial loading to the sediment. This tends to offset ongoing bacterial die-off and sediment transport and results in higher levels after sediment agitation in dry weather. However, the concentrations tend to decrease from source to downstream.

Mechanical sediment resuspension also increased levels of suspended sediments in the water column (Figs. 11, 12 and 13). The greatest effect was noticed at sites which had the lowest water column suspended sediment levels before sediment agitation. This would indicate that there is a higher rate of deposition occurring at these sites. James Gardens source site (Fig. 12) was an exception in that it exhibited the highest levels of suspended sediments both before and after sediment resuspension. There may be sufficient ongoing inputs of fecal material at this site to maintain high water column suspended sediment levels.

Intermediate Weather

During intermediate weather conditions (i.e. 24 to 48 hrs. after a rainfall event) the levels of both suspended sediments and fecal indicator bacteria in the water column fell somewhere between dry and wet weather concentrations. Once again it may be seen that the effect of the pollution inputs on the water column is not always evident prior to mechanical sediment resuspension. At Black Creek where the fecal indicator concentrations were lower than during dry weather, with the exception of fecal streptococci at source and downstream, it is possible that a flushing effect has occurred in the stream; the channel is

quite narrow and the creek exhibits a rapid increase in flow during wet weather. The level of suspended sediment in the water column decreases from upstream to source as well and this may be the result of increased deposition as the stream flow decreases after wet weather. Jenkins et al (21) also observed increased sedimentation in response to stream velocity decrease.

Mechanical sediment resuspension during intermediate weather caused increases in bacterial concentrations and suspended sediment levels, but again the increases at the Black Creek and Elhart Drive locations were not as high as those exhibited during wet weather. At James Gardens, the suspended sediment levels were higher during intermediate conditions in comparison with wet weather and, as previously indicated, this may be due to direct deposits of fecal material. The Elhart Drive bacterial concentrations measured post agitation during intermediate weather conditions were higher than the post agitation concentrations achieved in dry weather, possibly due to increased deposition after a rainfall. This was also true for the James Garden sites with the exception of the source site where the levels were slightly lower possibly because of washout of the freshly deposited fecal material during the higher wet weather flows. Lower levels at the Black Creek source and downstream sites, in comparison with dry weather post sediment agitation, may have been due to a washing and or scouring effect in the creek as a result of heavy rainfall.

Wet Weather

During wet weather, there were high levels of both fecal indicators and suspended sediments in the water column, but frequently the bacterial increase was proportionately greater than the suspended sediment increase. As during dry and intermediate weather conditions, the effect of the pollution inputs was somewhat obscured in the water column during wet weather due to high upstream contaminant levels and dilution. It is interesting to note that this obscuring effect occurs at Black Creek even though the combined sewer outfall exhibited concentrations of 1,500,000 fecal coliforms and 1,100,000 E. coli per 100 mL. The fecal coliform and E. coli levels from the Elhart Drive storm sewer effluent were lower due to dilution from storm runoff.

Fecal coliform to fecal streptococcus ratios tended to drop during wet weather even though there were fresh fecal inputs and higher fecal coliform and E. coli levels present. It is possible that streptococci from older or distant inputs are surviving in the sediments and are causing increases in the water column levels when sediments are agitated during storms. Additional streptococcal organisms from plant sources can also be washed into the river through storm runoff (30, 31). Other workers have suggested that the FC/FS ratio should be used with caution because of the differential die-off rates of the two indicators. Furthermore, the effect of environmental factors may alter their relationship and may lead to erroneous interpretation of the ratios (11, 32, 33).

Survival of Indicator Bacteria During Different Seasonal Conditions

The length of survival of E. coli under summer weather conditions (i.e. water temperature = 18 to 25°C) (Figs. 14, 15 and 16) was very short. Generally there was a 97 to 99% die-off rate within 24 hrs. with an equivalent or slightly lower rate occurring over day two and day three. At Black Creek, E. coli exhibited a lower die-off rate (i.e. 80.2% in 24 hrs.) which may be attributed to high nutrient loadings in the creek (average total Kjeldahl nitrogen loading to the lower Black Creek area is 16,494 g/day; average NH₃-N loading is about 9,305 g/day; and total phosphorus loading is approximately 2,394.4 g/day (33).

Streptococcus faecalis var liquefaciens tended to survive somewhat better during summer conditions except at the Elhart Drive location where it decline more rapidly than E. coli. Dutka and Kwan (34) also found the E. coli survival response to be much greater than S. faecalis in Lake Ontario waters. S. faecium exhibited a slower die-off rate than either S. faecalis or E. coli during the summer. This bacterium has been known to survive for more than 28 days in surface waters (29).

Under winter conditions (average water temperature = 6 to 9°C (Figs. 17, 18, and 19) the survival response of all three indicator bacteria increased. For E. coli, the initial 24 hr. percent die-off rate decreased at both the James Gardens and Black Creek sites and increased at the Elhart Drive site. However, during the second and third day the E. coli die-off rate

decreased dramatically at the Elhart Drive and Black Creek locations. By day three, the die-off rate for E. coli had increased to 100% at the Black Creek site.

S. faecalis and S. faecium were found to have similar die-off rates during winter conditions. It has been suggested that S. faecium survives longer than S. faecalis in warmer polluted waters, but that both organisms assume closer rates of decline in colder or pristine waters (Dufour, personal communication, 1985). S. bovis exhibited a very rapid die-off rate (i.e. greater than 99% in 24 hrs.) during the winter. Similar rates have been reported for this bacterium under summer conditions (28). Unlike other members of the fecal streptococcus group that may be recovered from environmental sources, S. bovis is specific to the feces of certain warm blooded animals (35). Its rapid die-off indicates that a recovery of this organism from surface waters is indicative of recent animal fecal inputs.

Although in situ survival of other members of the coliform group (i.e. Enterobacter and Klebsiella) was not studied at the three locations, previous investigations have shown that these bacteria can persist in surface waters for longer periods than E. coli (29,36). The ability of these species to utilize internal endogenous reserves may aid in increasing their survivability in surface waters. The fact that some members of these above mentioned species are encapsulated may also enhance their survival (29).

Regrowth of coliforms in waters enriched by sewage, food processing plant and pulp and paper mill effluents has also been reported (37,38), as well as regrowth in sediments and soils (39,40). Since a differential die-off rate occurs among members of the coliform group, the proportion of E. coli in fecal coliform populations will decrease with time. Thus the E. coli to fecal coliform ration (EC/FC ratio) may be a good indication of the age of the contamination.

Summary

A comparison of the overall average increase in bacterial concentration and sediment weight during dry and intermediate weather conditions caused by sediment agitation at the three locations is presented in Table 1. The increase in water column bacterial concentrations from dry to wet weather as well as the percent die-off in 24 hrs. at each location is also given.

The greatest increases in both sediment, fecal coliform, and E. coli levels during dry and intermediate weather were obtained in the Humber River at James Gardens. It would thus appear that this location has the greatest potential for deposition under these weather conditions possibly because of the shallowness of the water column in this area. The high concentration of bacteria in the sediment is due to the continuous fecal input from waterfowl, with the possibility of further contributions from upstream loadings to this location. Although the die-off rate of E. coli was highest at this location (i.e. 99.96% in 24

hrs.), it is possibly off-set by the magnitude of the ongoing contaminant inputs.

At Elhart Drive the dry weather increases in recovery of fecal indicator bacteria were considerably lower than at James Gardens but higher than at Black Creek. The E. coli die-off rate was second highest at this location, again suggesting that continuous inputs of bacteria can off-set high die-off rates allowing for accumulation in the sediments under dry conditions. The decreased level of sediment bacterial accumulation in comparison with James Gardens is most likely due to factors such as lower upstream loadings, less sediment deposition, and the nature of the input at this location (i.e. storm sewer outfall as apposed to direct fecal input).

Combined sewer outfalls such as the Hyde Avenue outfall are a major source of bacterial contaminants to Black Creek during wet weather. The greatest increase in bacterial concentrations from dry to wet conditions was observed at this location with fecal coliforms and E. coli exhibiting increases of 12,738 and 7,628 bacteria per 100 mL, respectively. The increased recoveries obtained after sediment agitation during intermediate weather are possibly related to high loadings during the preceding storm event, and better survival of indicator bacteria in Black Creek.

During dry weather, the Black Creek location exhibited the lowest sediment accumulation of bacteria. This probably due to minimal contaminant input during dry weather, a lower rate of

sediment deposition, and the adsorption characteristics of the sandy sediments at this location. The problems associated with using relative proportions of fecal coliforms to fecal streptococci (i.e. FC/FS ratio) in stream becomes obvious when comparing the three locations. For example, there is little variation in the ratio during dry weather at the three locations. Furthermore, the highest ratio was obtained at James Gardens where the fecal input is known to be of non-human origin. During wet weather, as previously mentioned, the relative concentration of fecal coliforms to fecal streptococci decreases at all locations due to resuspension of older or distant inputs. The differential die-off rates of the two indicators would account for the survival of fecal streptococci in older inputs.

Conclusions

Bactereial exchange between the sediments and the water column does occur when sediments are resuspended; however, the extent to which this process occurs depends upon the survey location (i.e. type of pollution input), the sampling site at a given location (i.e. relative to the input), the flow rate of the river, prevailing weather conditions, and the bacterial parameter being analyzed.

The results of this study indicates that the greatest accumulation of contaminants in the sediment occurs at locations where sediment deposition is combined with continuous high level pollution input. The greatest local impact appears to be in

areas receiving direct fecal deposits. However, the overall degradation of water quality in the Humber River watershed appears to be due to the cumulative effect of a large number of different sources; localized effects are not indicative of the impact of any one pollution type on the entire water course.

In determining the source of the pollution (i.e. human or non-human), it is necessary to develop an interpretive methodology combining information obtained from different types of data (eg. site observation, upstream inputs, bacterial concentrations and species). Reliance on one piece of information, such as the FC/FS ratio, is not sufficient. Interpretive tools such as EC/FC ratios however, may be useful in determining the age of a pollution input.

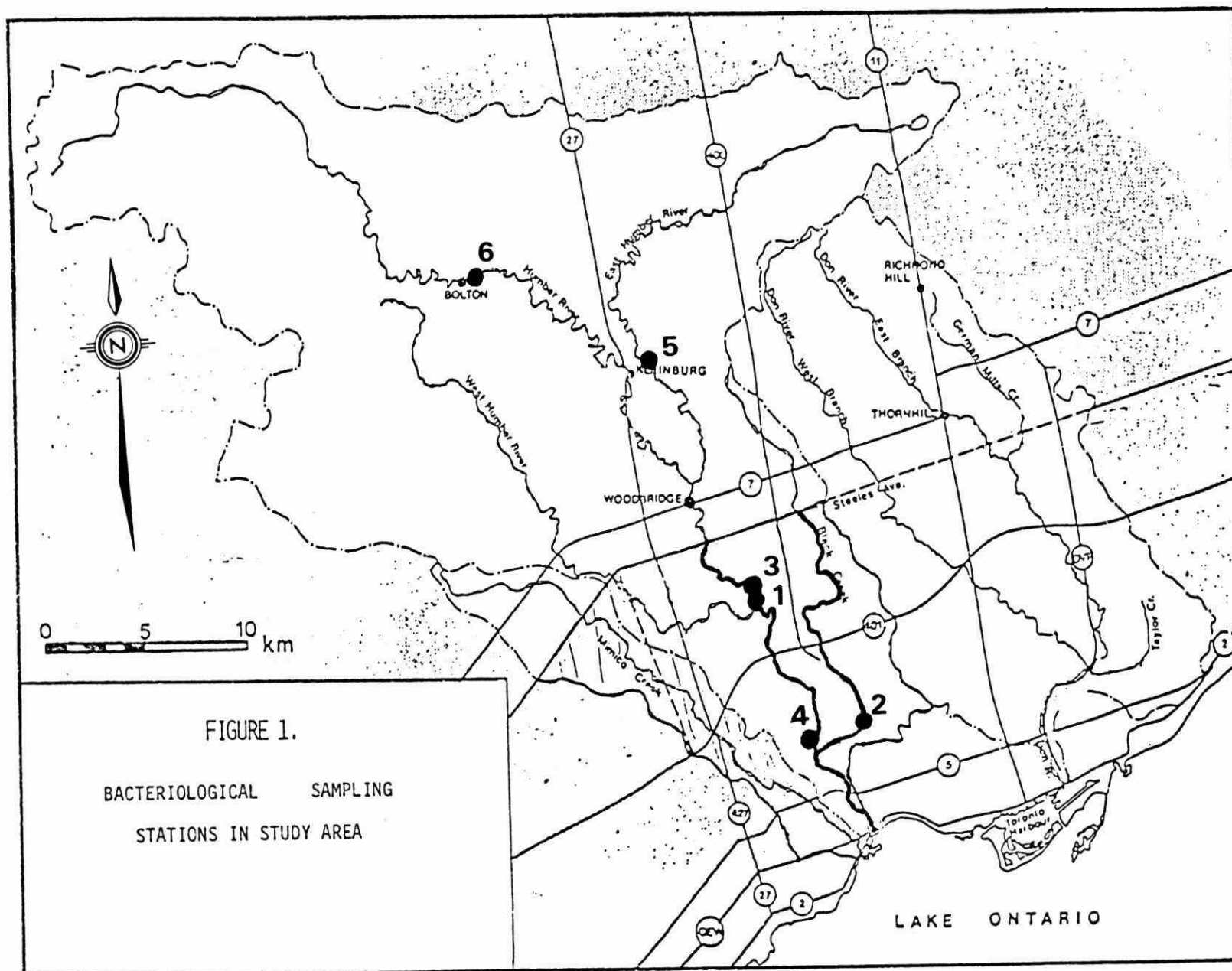


FIGURE 2 IMPACT OF ELHART DRIVE STORM SEWER ON IN STREAM FECAL COLIFORM CONCENTRATIONS

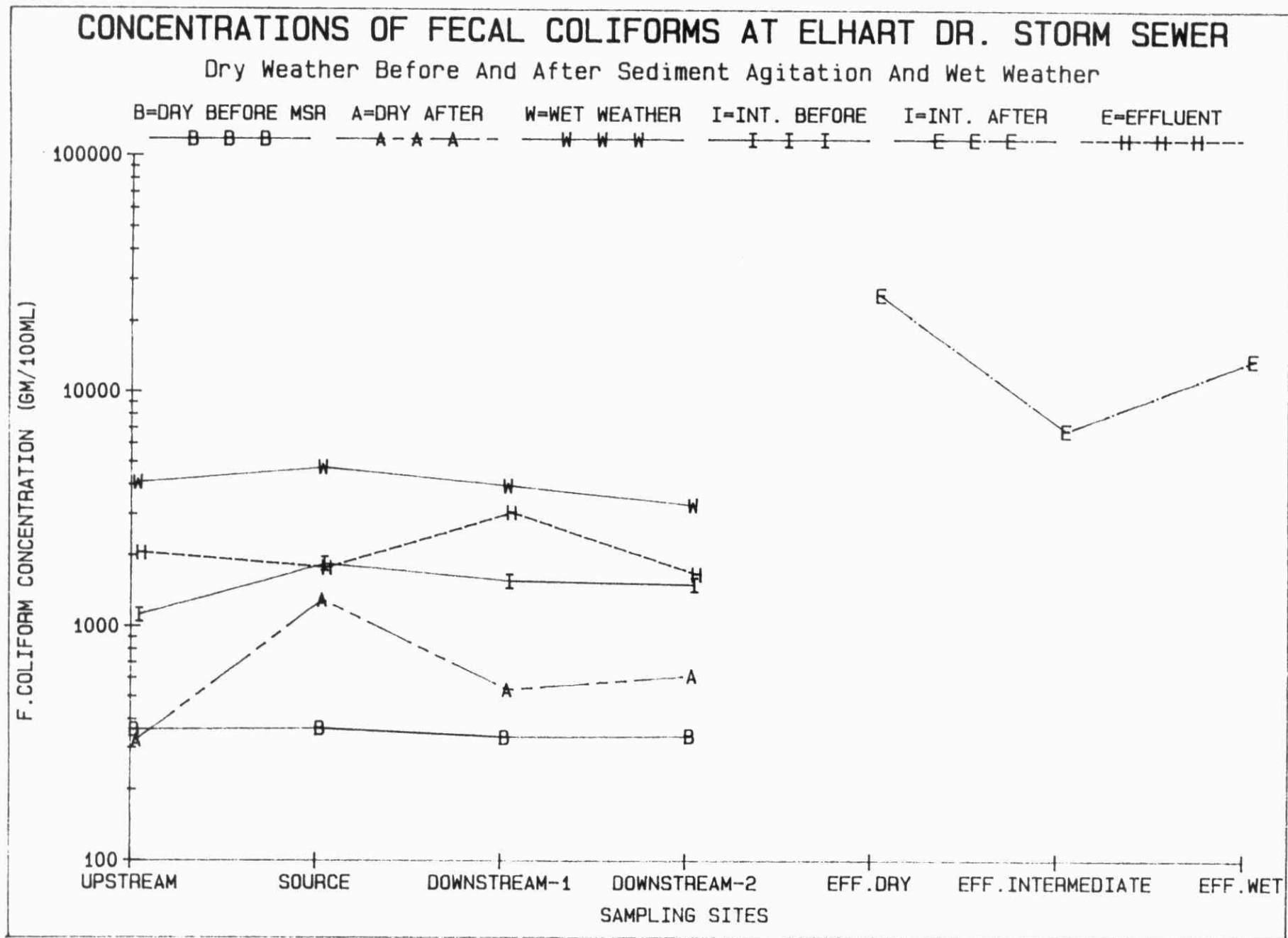


FIGURE 3: IMPACT OF ELHART DRIVE STORM SEWER ON IN STREAM E. COLI CONCENTRATIONS

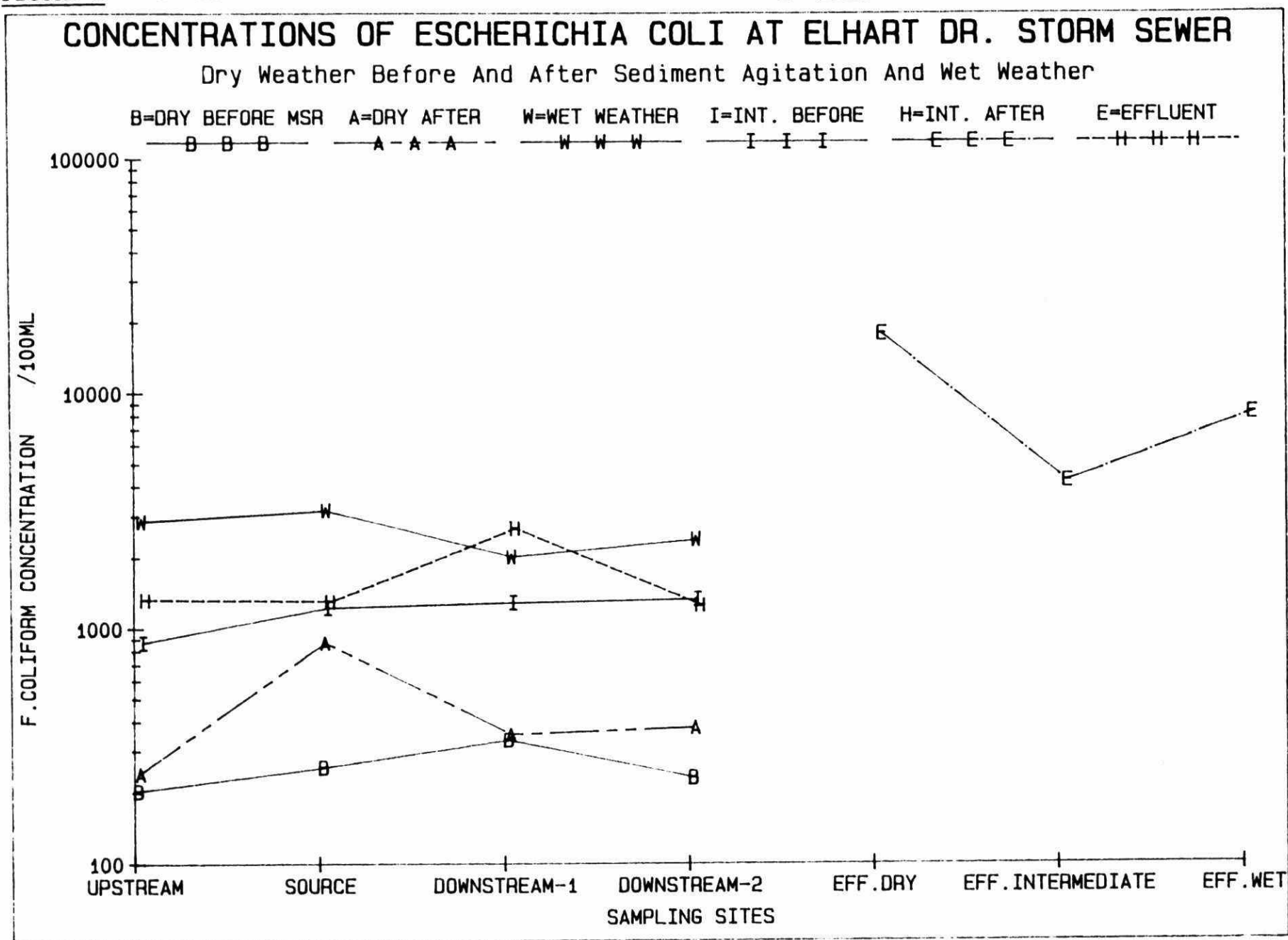


FIGURE 4: IMPACT OF ELHART DRIVE STORM SEWER ON FECAL STREPTOCOCCI CONCENTRATIONS

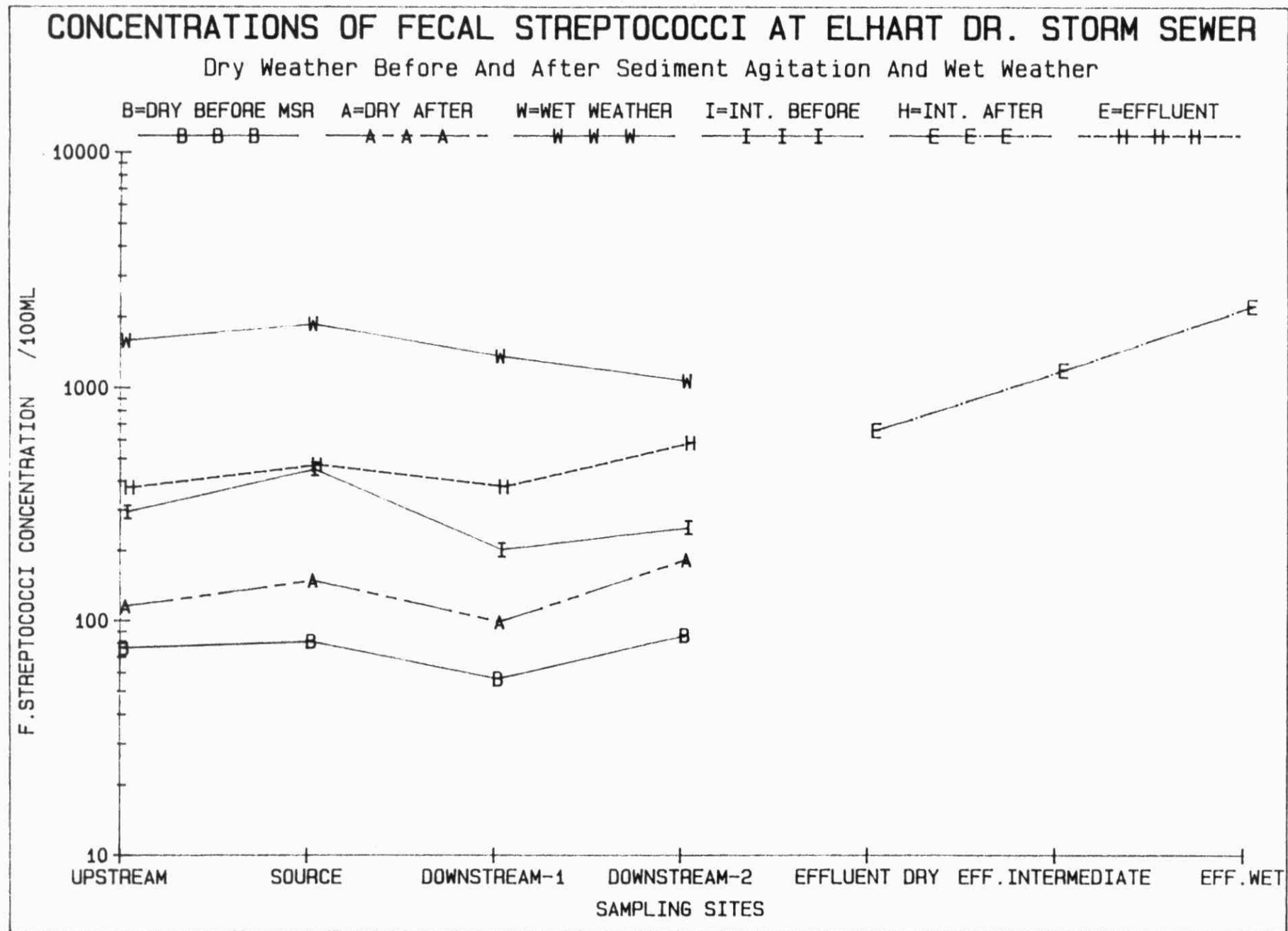


FIGURE 5: IN STREAM FECAL COLIFORM LEVELS AT JAMES GARDENS

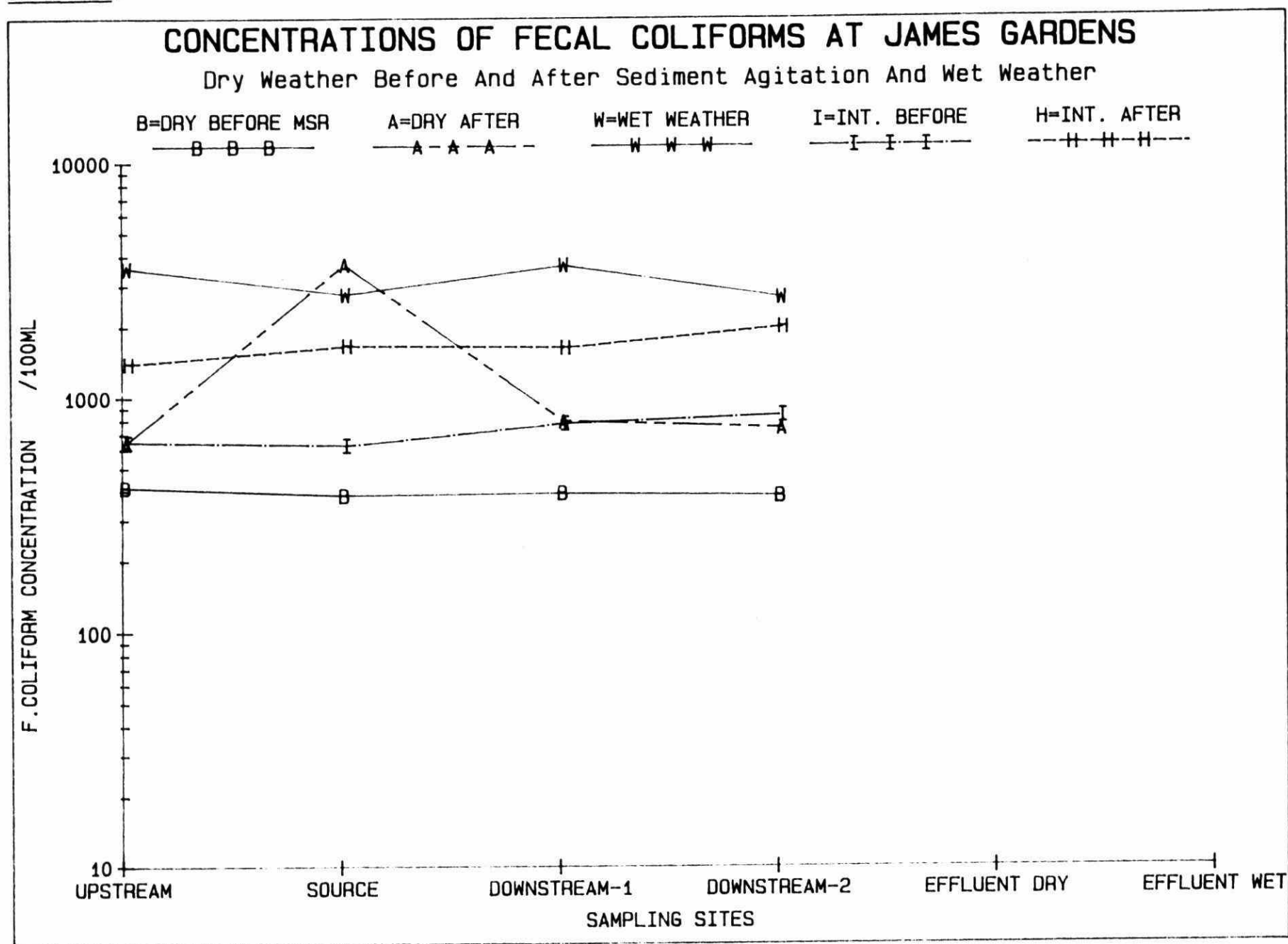


FIGURE 6: IN STREAM E. COLI CONCENTRATIONS AT JAMES GARDENS

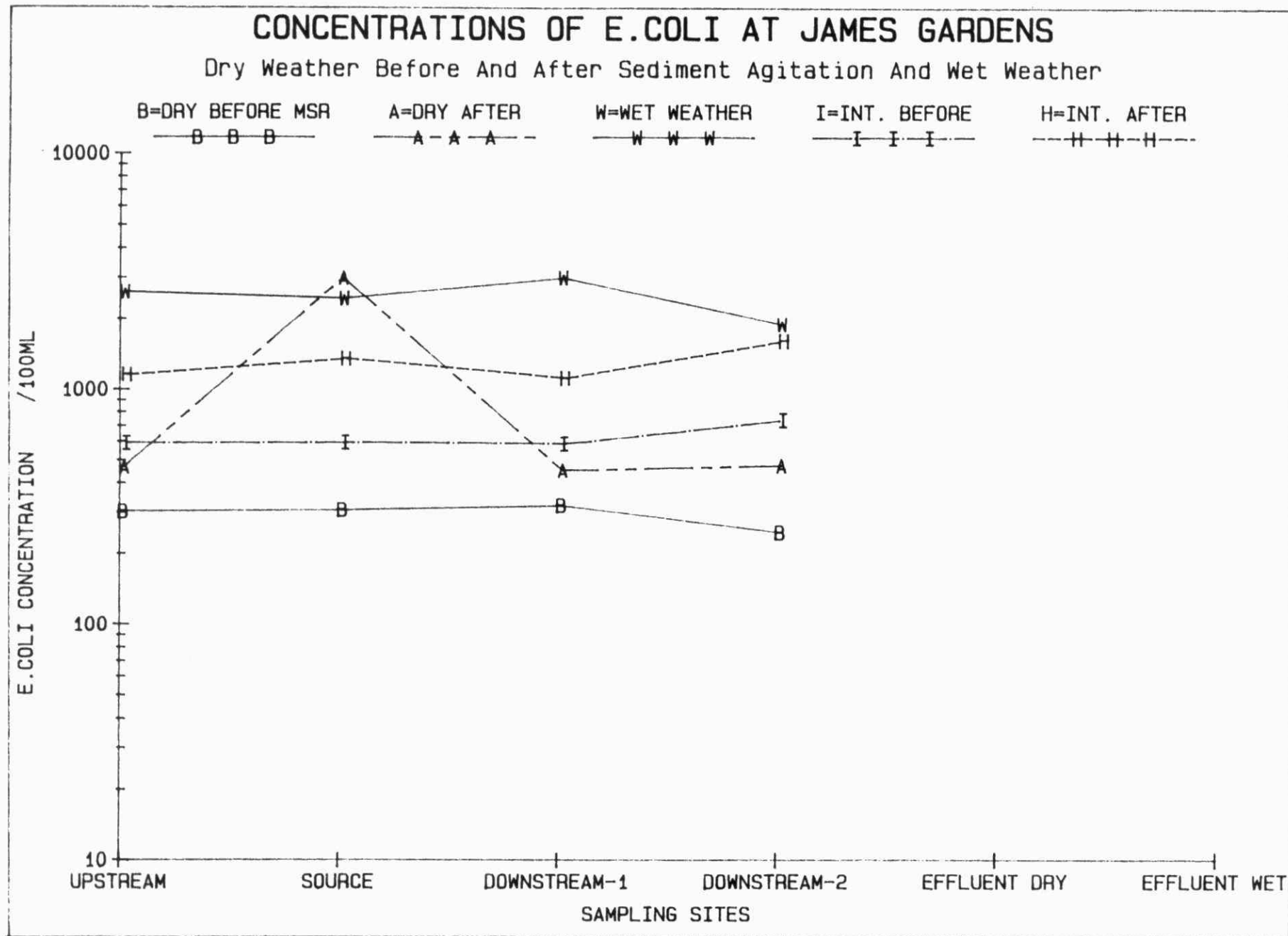


FIGURE 7: IN STREAM FECAL STREPTOCOCCI LEVELS AT JAMES GARDENS

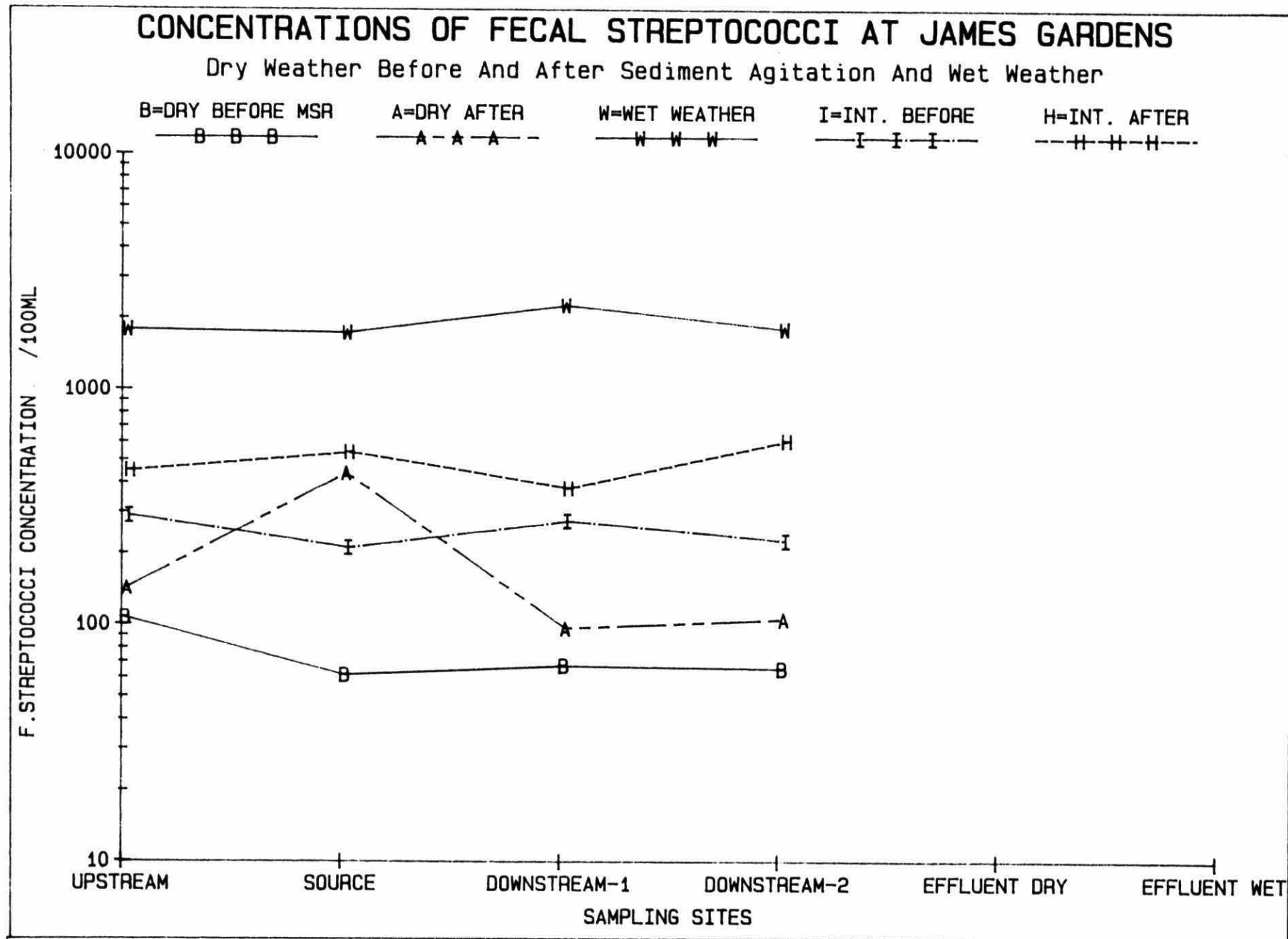


FIGURE 8: IMPACT OF BLACK CREEK COMBINED SEWER OUTFALL ON IN STREAM FECAL COLIFORM CONCENTRATIONS

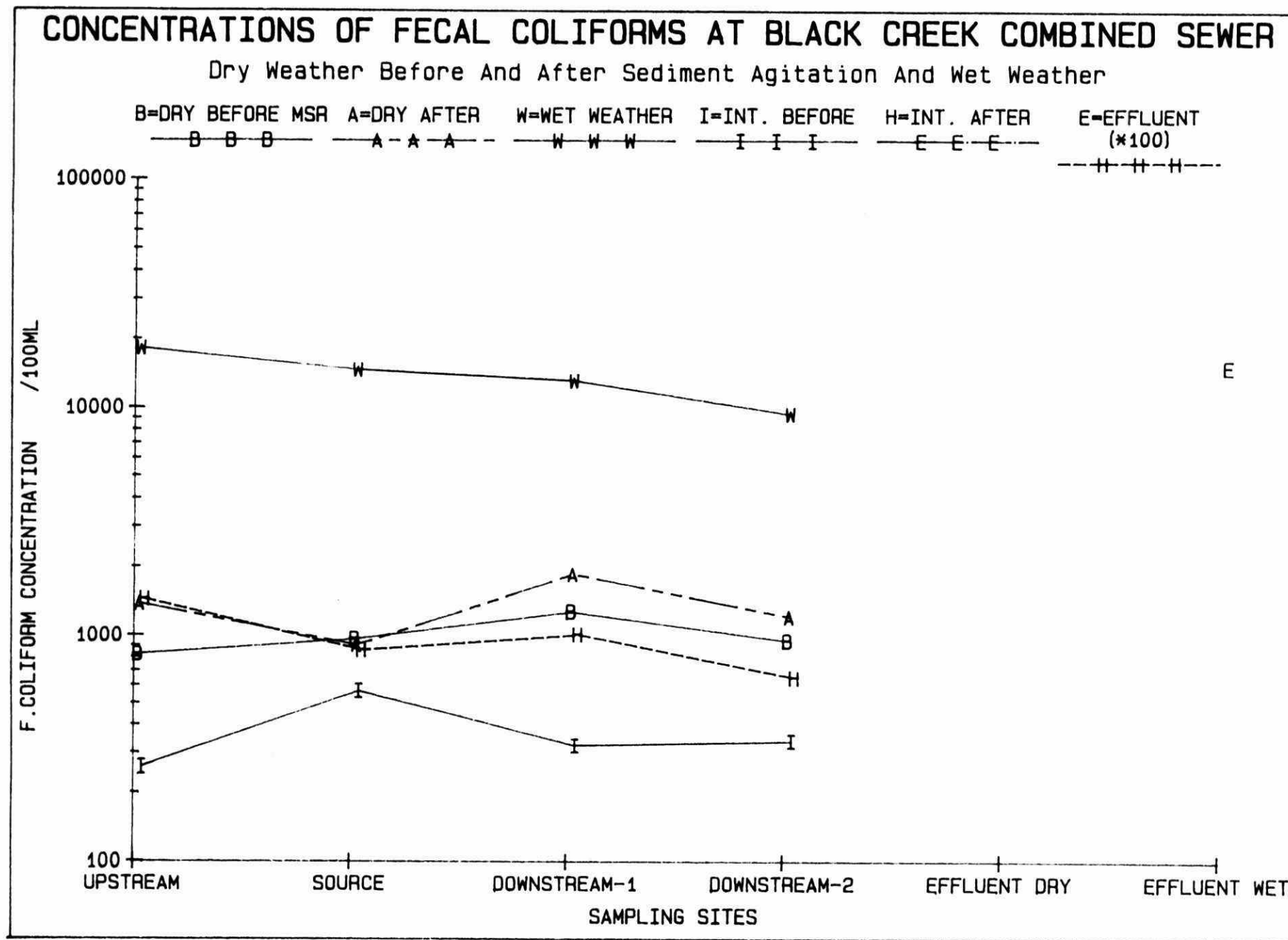


FIGURE 9: IMPACT OF BLACK CREEK COMBINED SEWER OUTFALL ON IN STREAM E. COLI CONCENTRATIONS

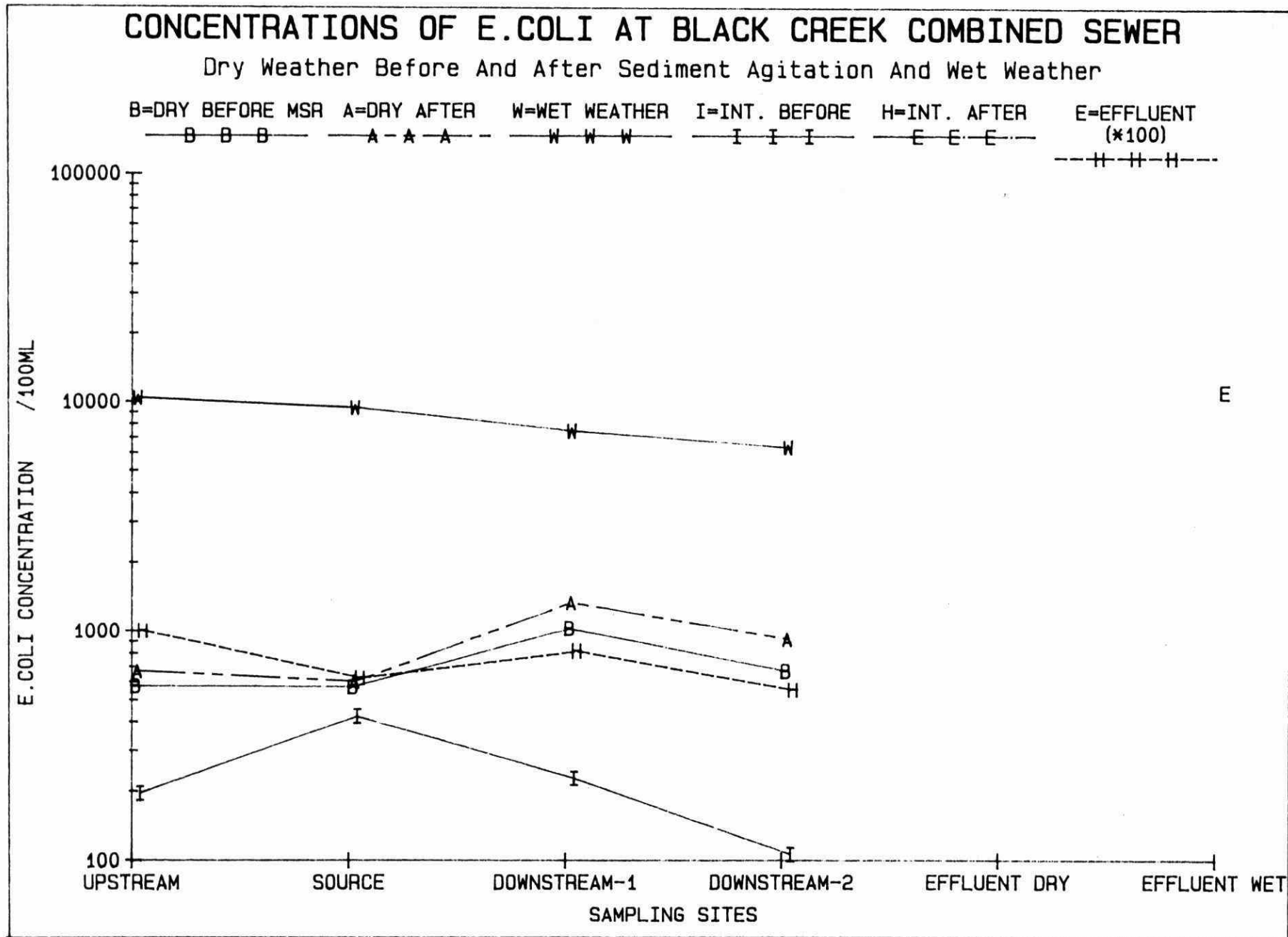


FIGURE 10: IMPACT OF BLACK CREEK COMBINED SEWER OUTFALL ON IN STREAM FECAL STREPTOCOCCI LEVELS

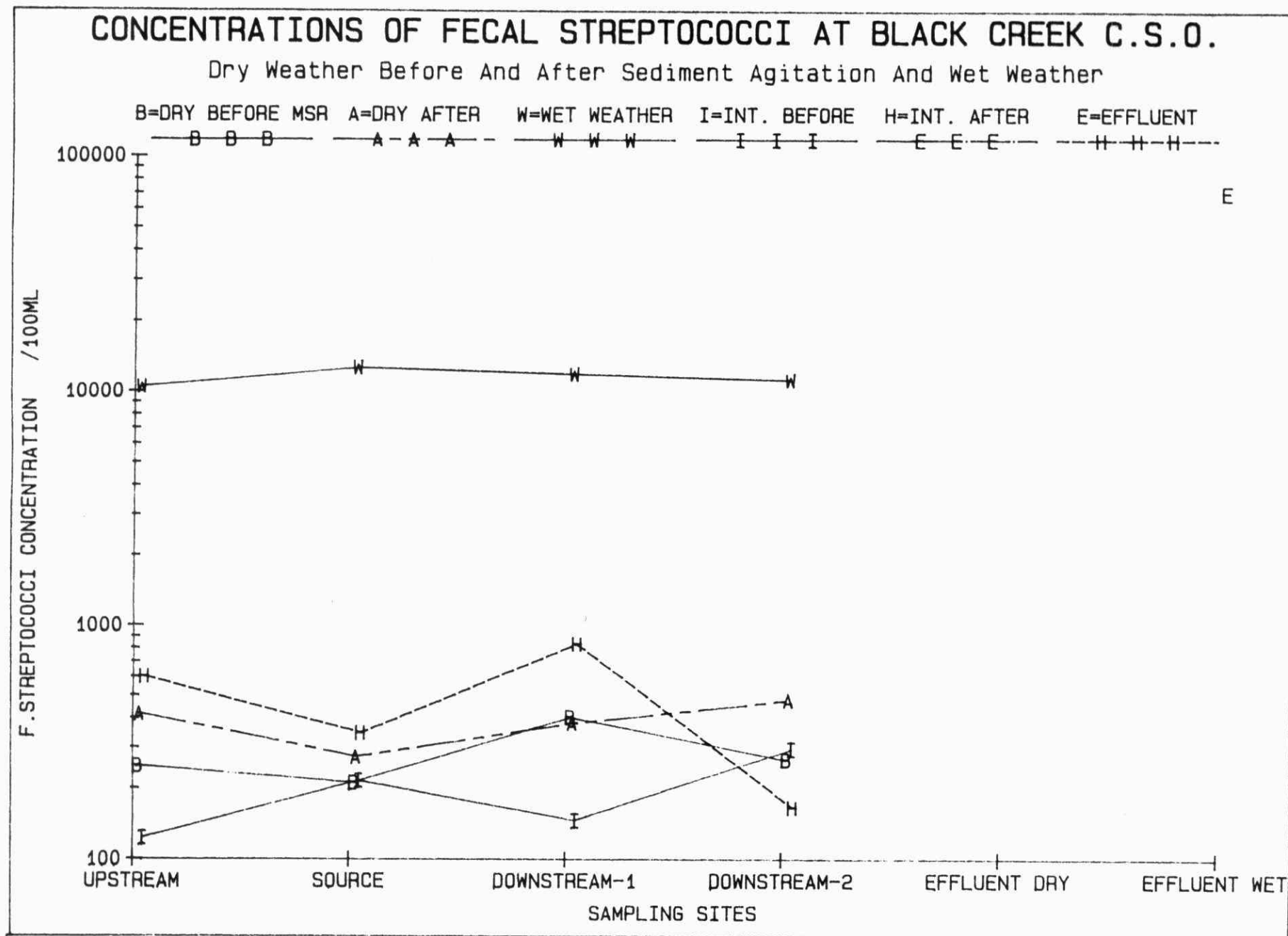


FIGURE 11: LEVELS OF SUSPENDED SEDIMENT AT THE ELHART DRIVE LOCATION UNDER DIFFERENT WEATHER CONDITIONS.

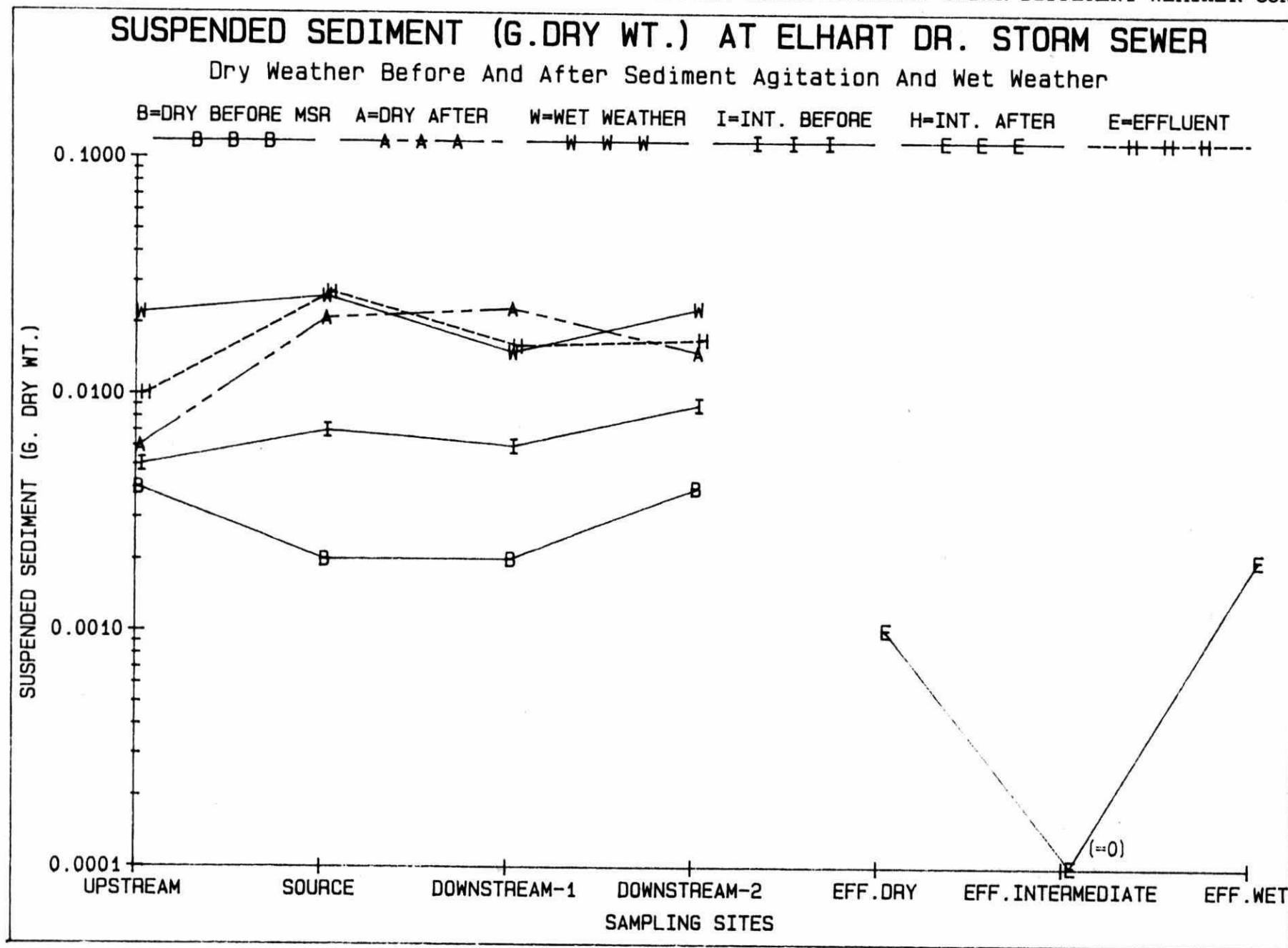


FIGURE 12: EFFECT OF WEATHER ON THE SUSPENDED SEDIMENT MEASUREMENTS AT THE JAMES GARDENS SITES

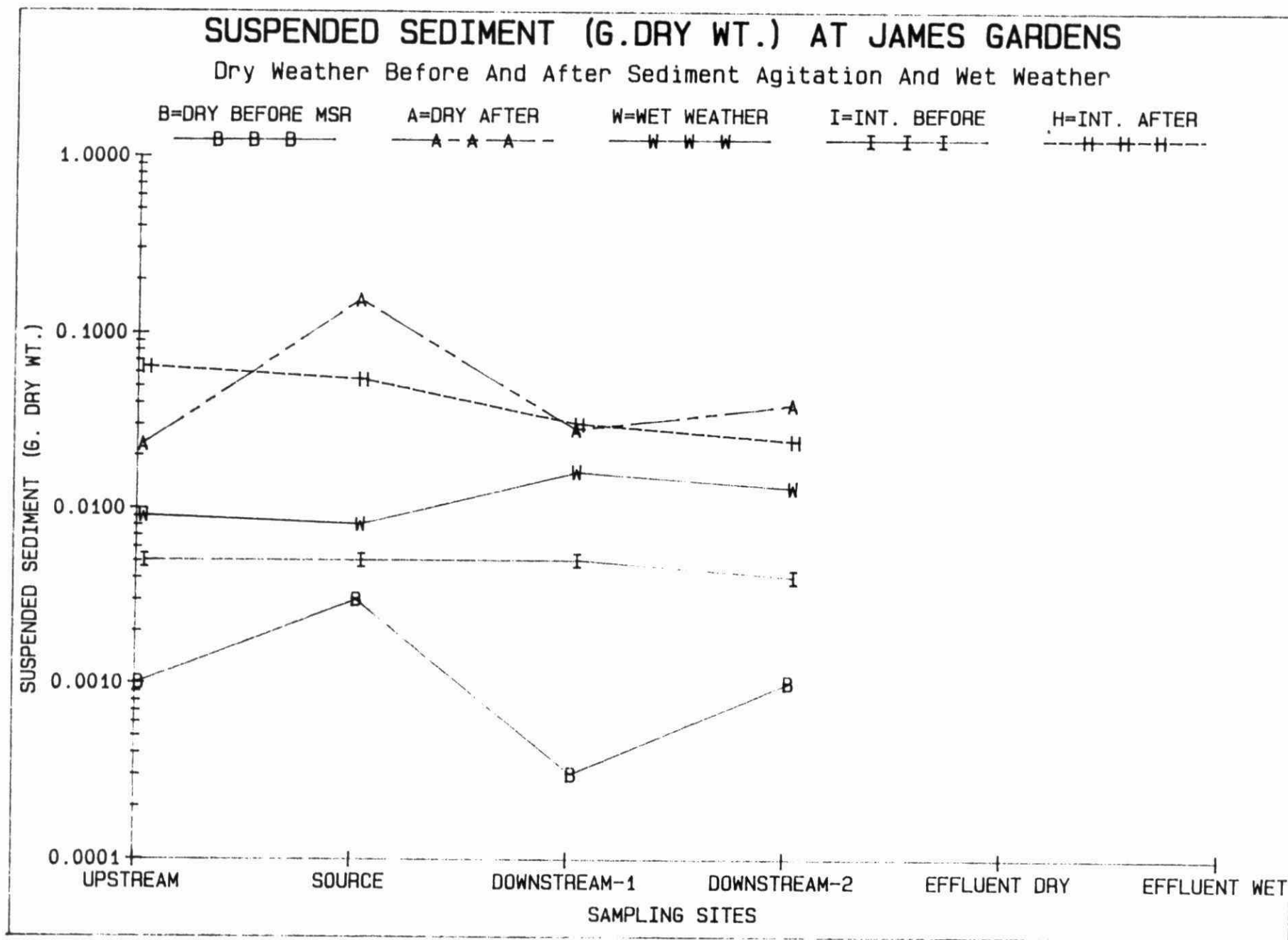


FIGURE 13: BLACK CREEK SUSPENDED SEDIMENT LEVELS UNDER DIFFERENT WEATHER CONDITIONS.

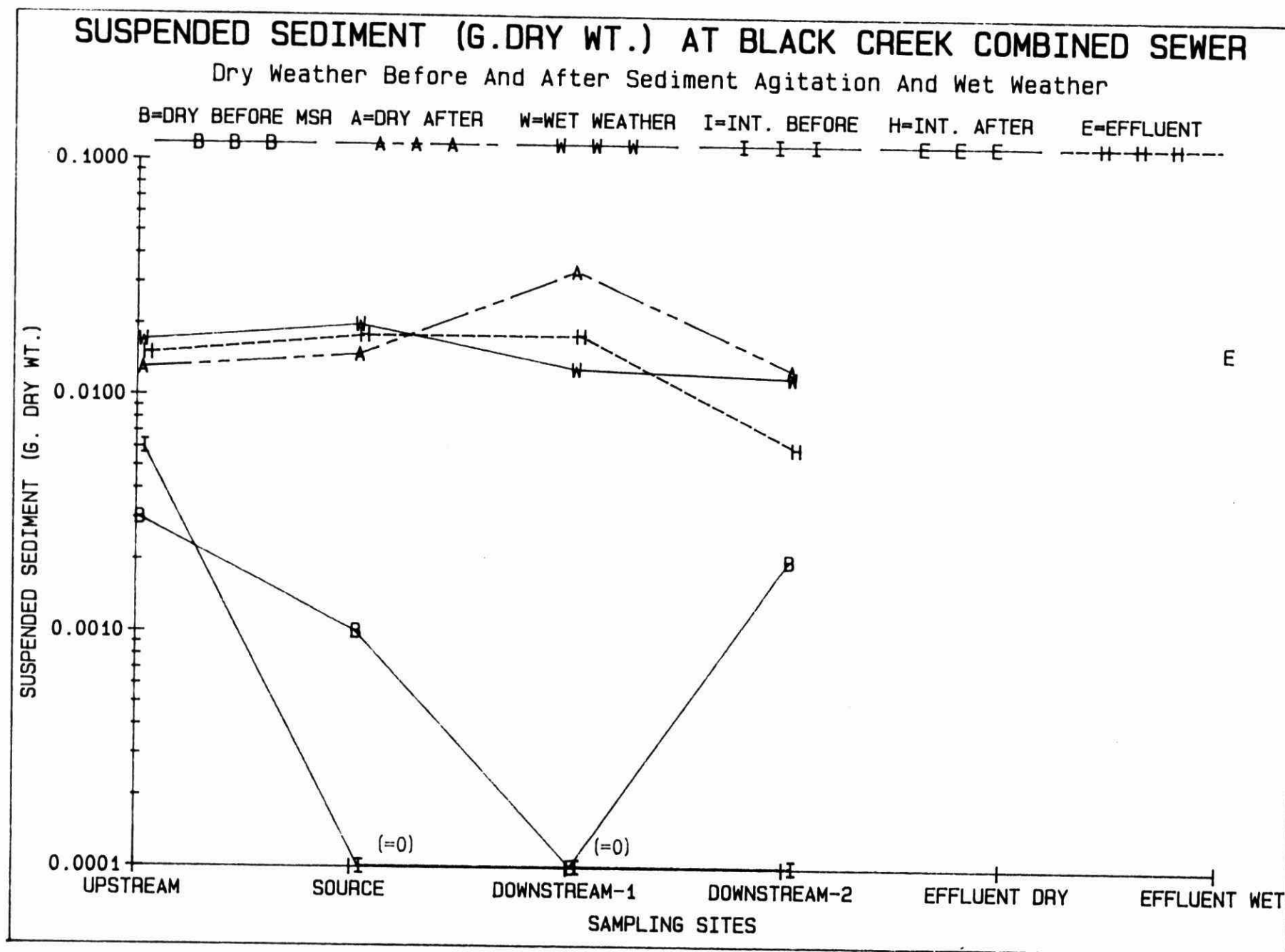


FIGURE 14: SUMMER DIE-OFF RATES OF FECAL INDICATOR BACTERIA AT THE ELHART DRIVE SITE

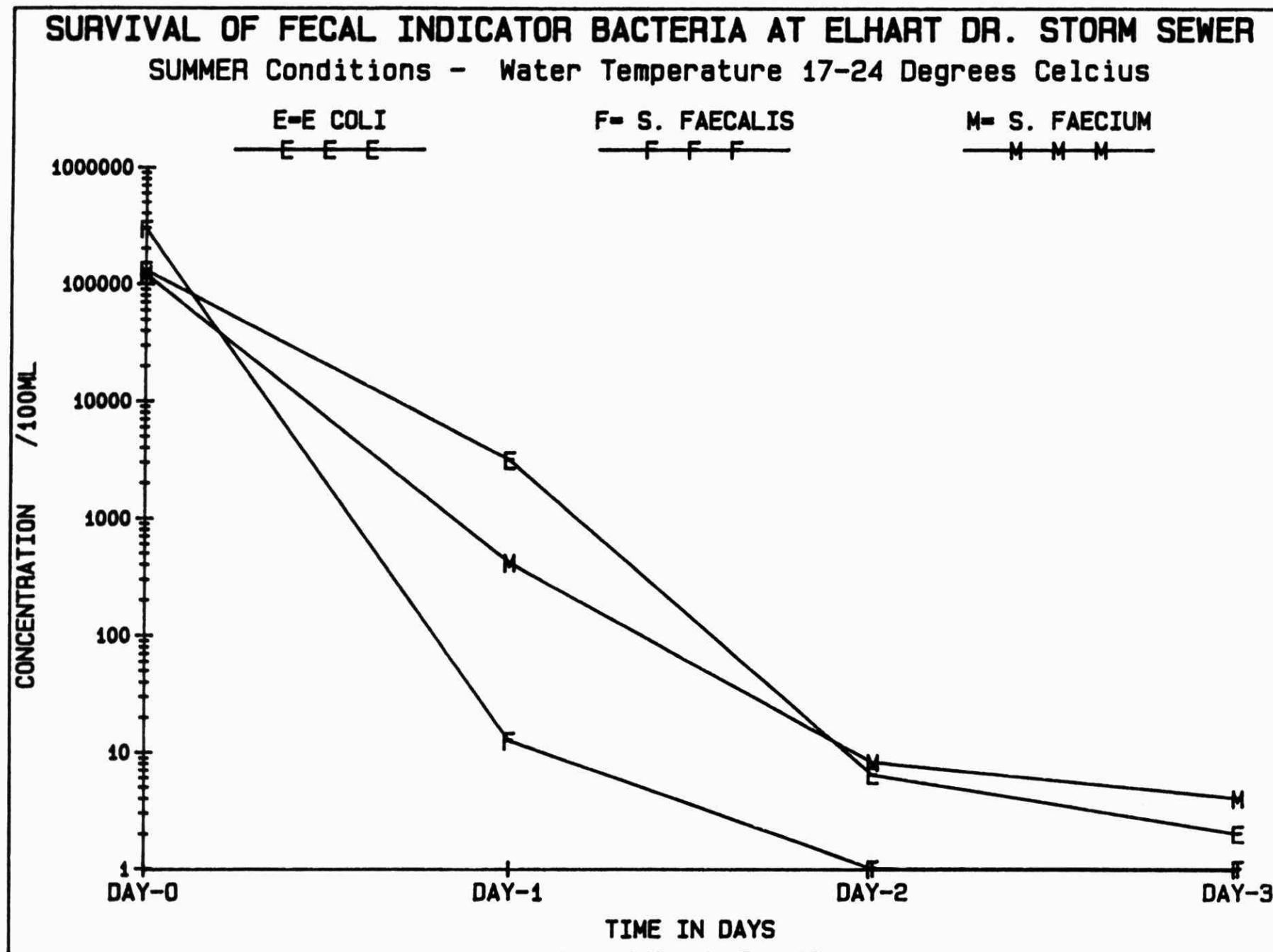


FIGURE 15: SURVIVAL RATES OF FECAL INDICATOR BACTERIA AT THE JAMES GARDENS LOCATION IN SUMMER

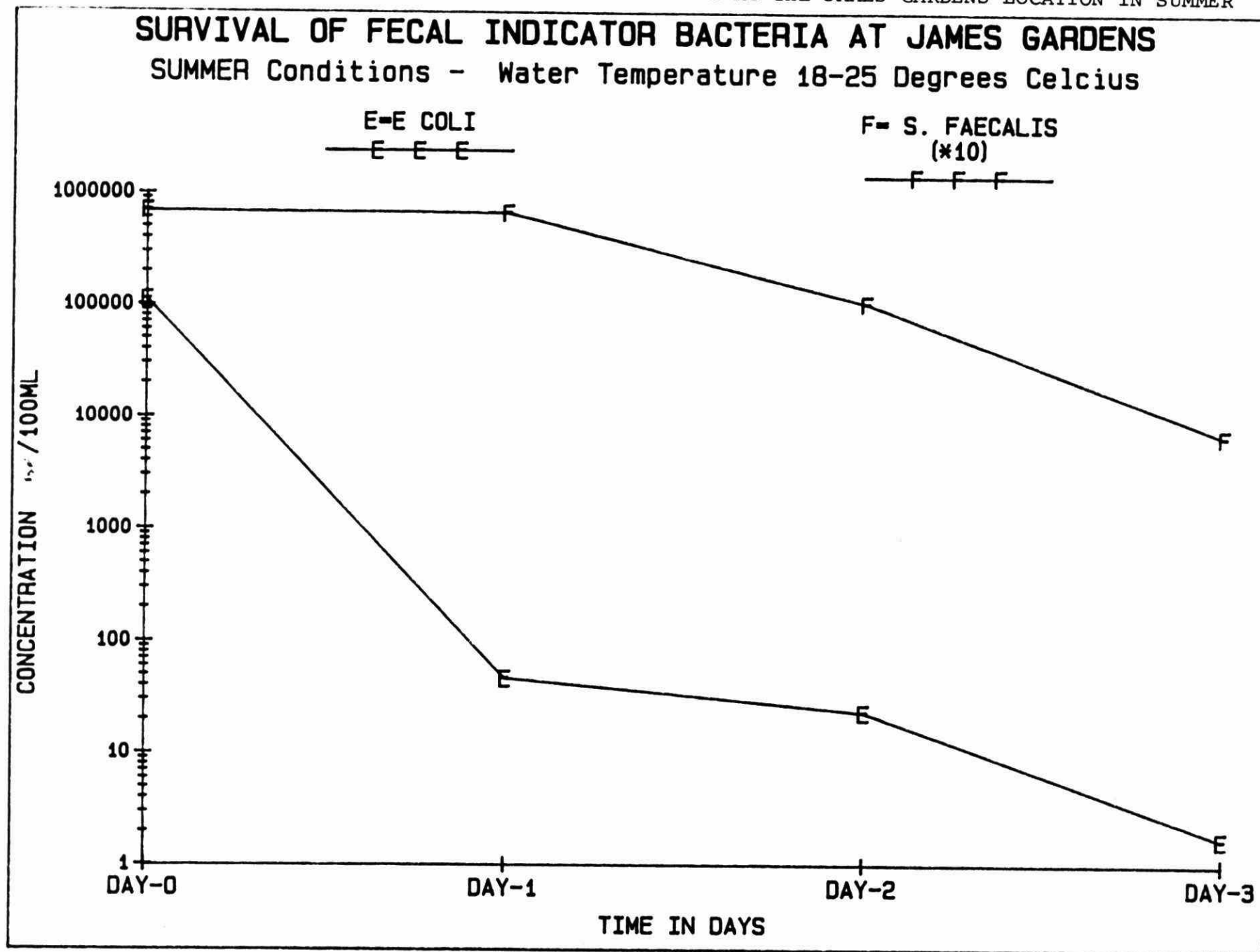


FIGURE 16: SUMMER SURVIVAL RATE OF FECAL INDICATOR BACTERIA AT THE BLACK CREEK SITE

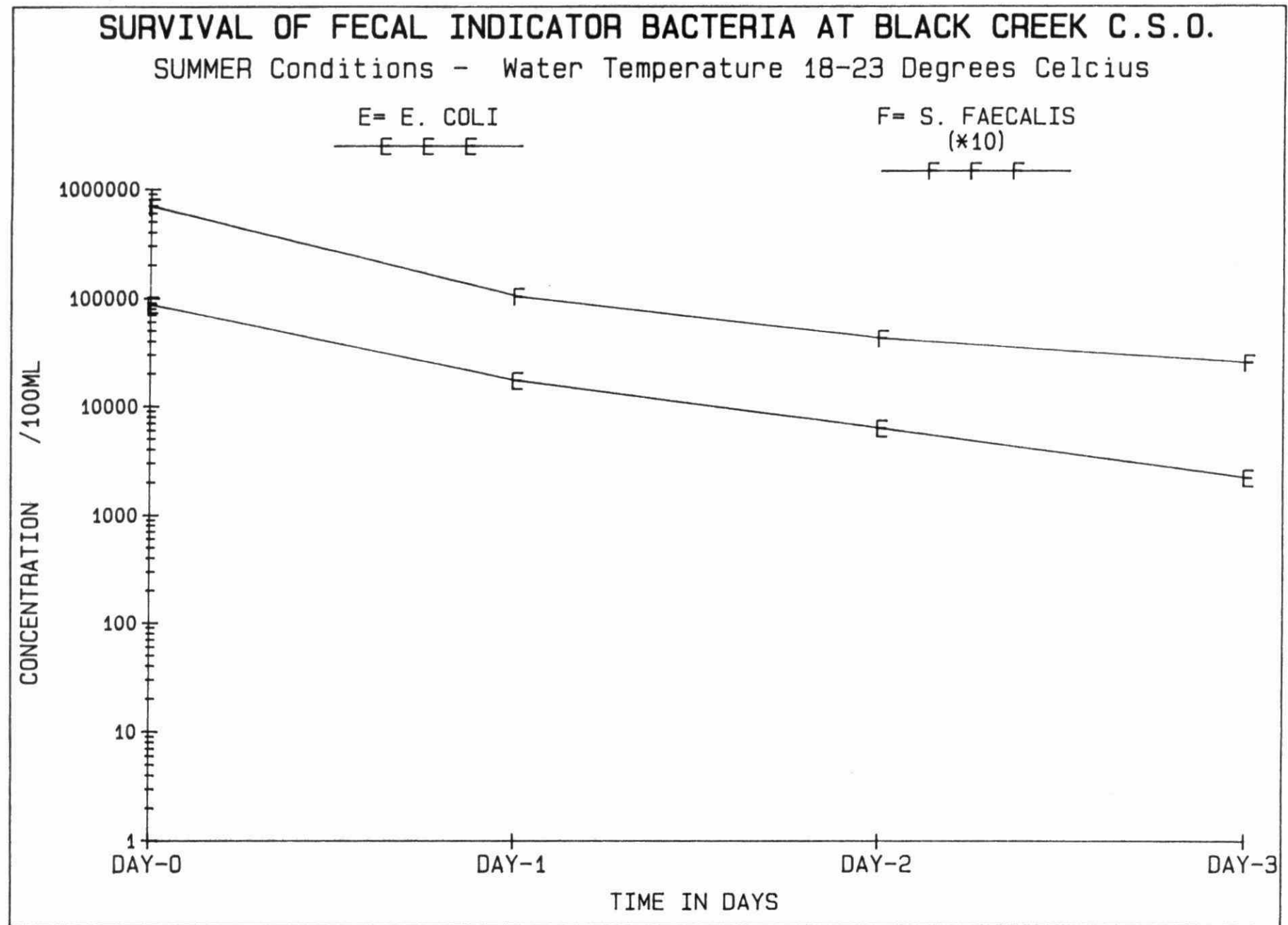


FIGURE 17: RATE OF SURVIVAL OF INDICATOR BACTERIA AT ELHART DRIVE IN WINTER

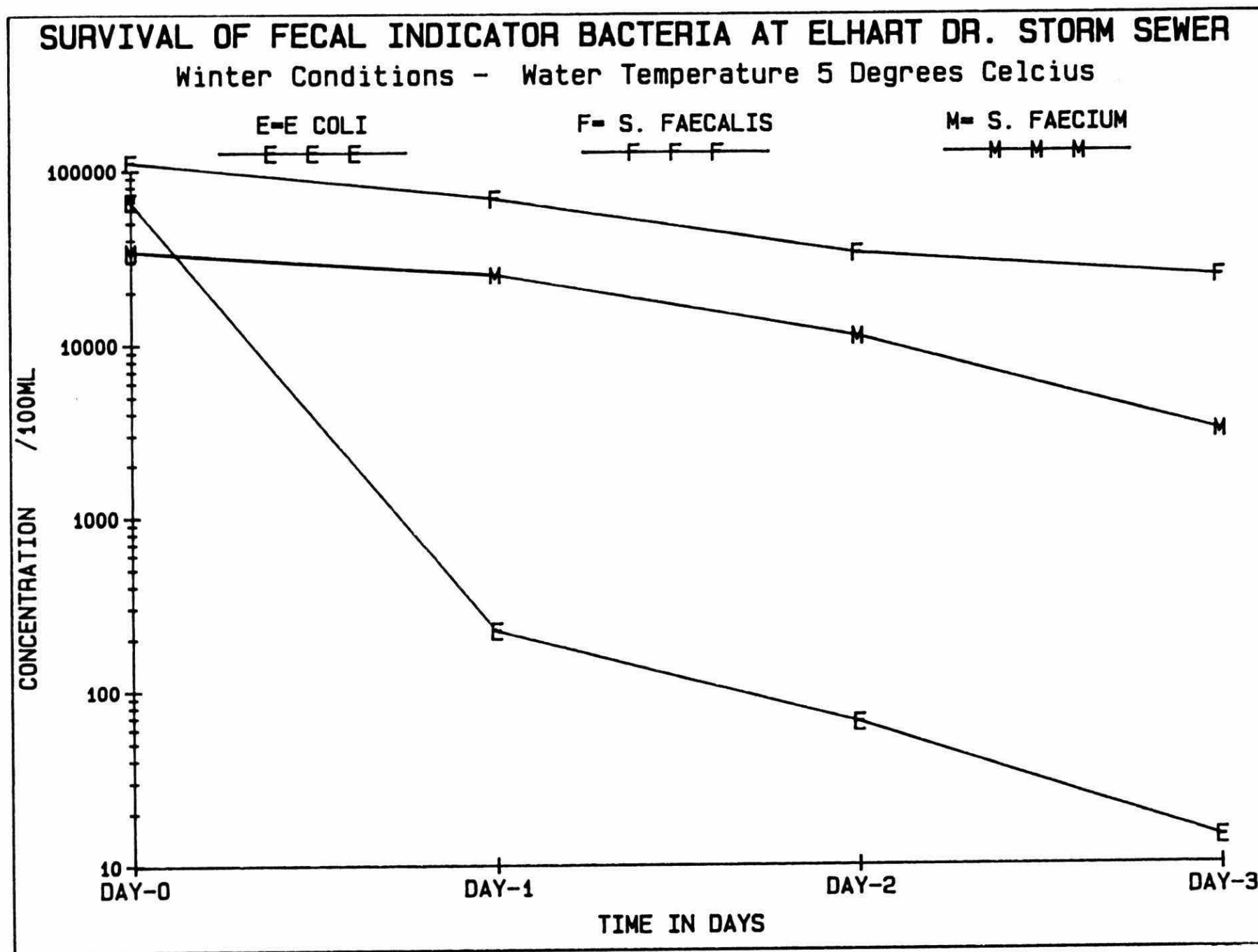


FIGURE 18: WINTER DIE-OFF RATES OF INDICATOR BACTERIA AT JAMES GARDENS

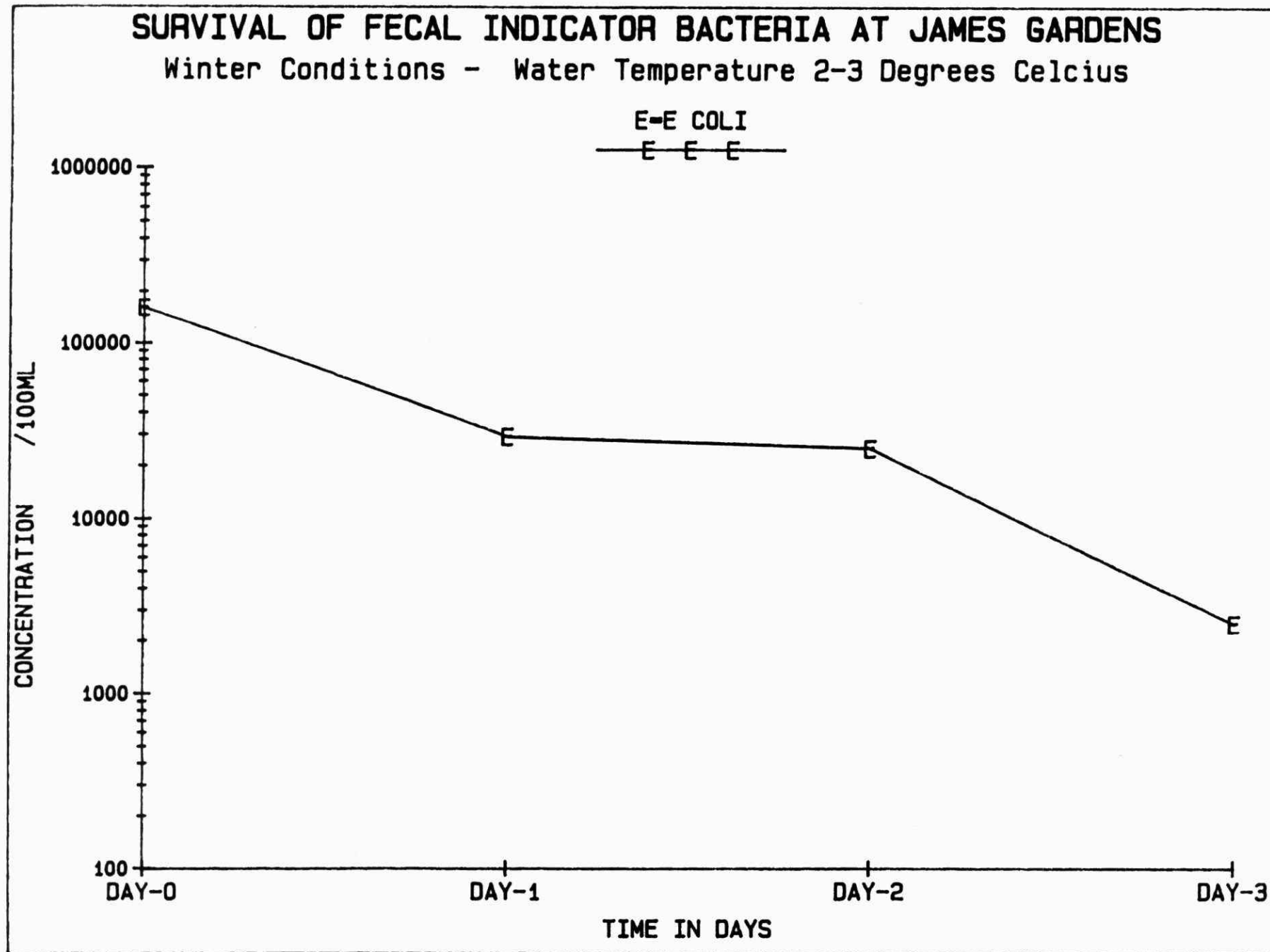


FIGURE 19: DIE-OFF RATE OF FECAL INDICATOR BACTERIA AT THE BLACK CREEK LOCATION IN WINTER

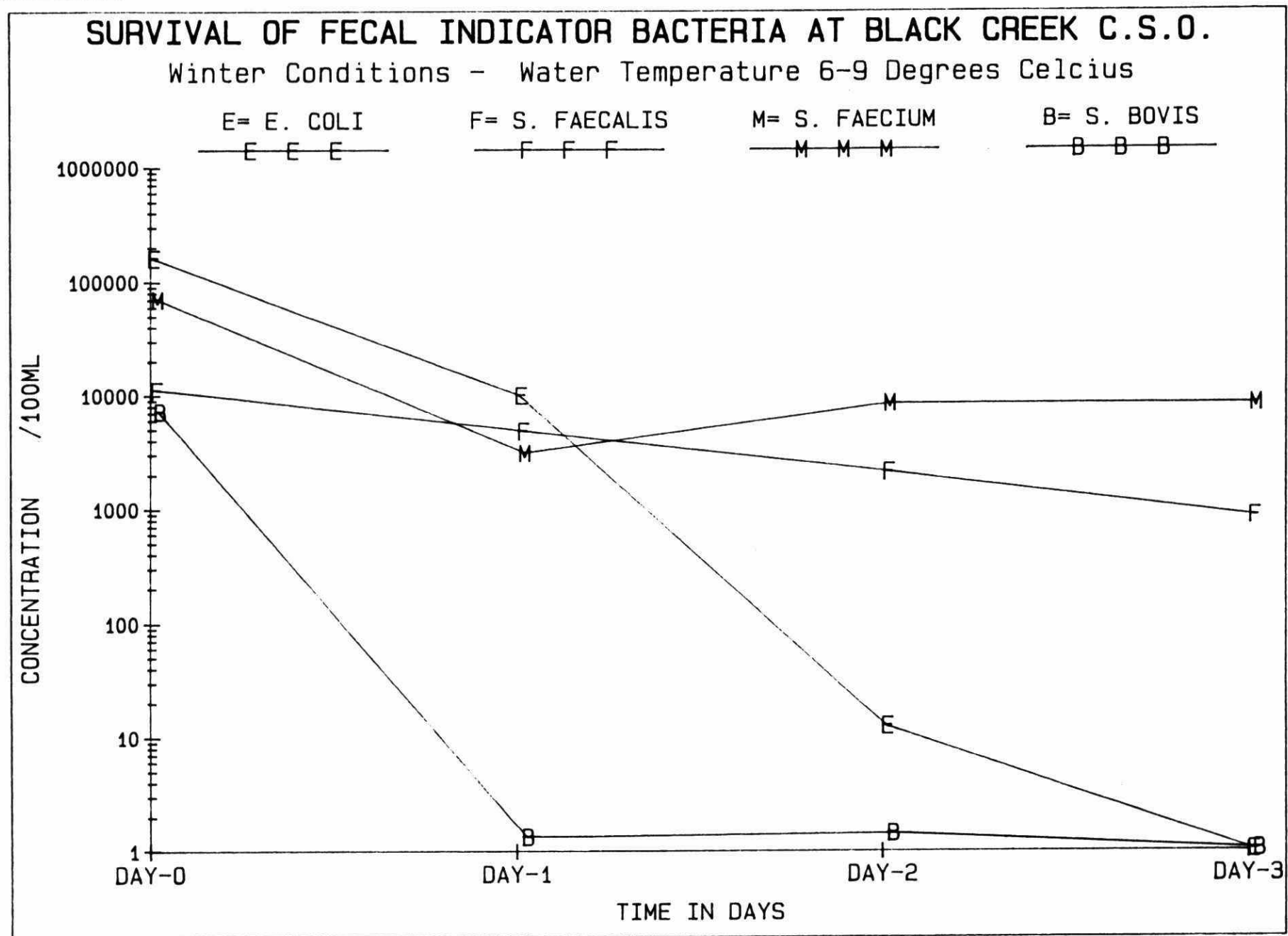


TABLE 1: Comparison of the Sampling Locations with Respect to Average Increases in Bacterial Concentration and Sediment Weight During Dry and Intermediate Weather (after Sediment Agitation) and from Dry to Wet Weather as well as Bacterial Die-off Rates During Summer and Winter Conditions

Location and weather condition	Parameter per 100 mls Sample				Flow Rate cm ³ /sec.	Percent Die-off Rate in 24 hours					
	Sed. wt. (grams)	FC	EC	FS		<u>E. coli</u> summer	<u>E. coli</u> winter	<u>S. faecalis</u> summer	<u>S. faecalis</u> winter	<u>S. faecium</u> summer	<u>S. faecium</u> winter
<u>Elhart Dr.</u>											
Δ Dry	0.013	341	203	136	1.660	97.7	99.7	99.99	38.2	99.7	26.5
Δ Int.	0.011	626.5	446.5	150.5	2.570						
Δ Dry to Wet	0.019	3651	2337	1389	2.552						
<u>Black Cr.</u>											
Δ Dry	0.017	330	168.5	104.5	0.152	80.2	93.8	85.0	56.3	-	55.7
Δ Int.	0.013	613	508.5	288	0.221						
Δ Dry to Wet	0.014	12738	7628	11226	0.284						
<u>James Gds.</u>											
Δ Dry	0.059	1074	801	120.5	2.593	99.96	81.9	2.9	-	-	-
Δ Int.	0.038	949	680	243	3.193						
Δ Dry to Wet	0.010	2758	2181	1818	4.468						

REFERENCES

1. Sayler, G.S. 1985. Distribution and significance of fecal indicator organisms in the upper Chesapeake Bay. Appl. Microbiol. 30: 625-638.
2. Zobell, C.E. 1943. The effect of solid surfaces upon bacterial activity. J. Baterial. 46: 39-56.
3. Taga, N. and O. Matsuda, 1984. "Bacterial Populations Attached to Plankton, Detritus in Seawater" from Effect of the Ocean Environment on Microbial Activities. Colwell, R.R. Ed., University Park Press, p. 433-448.
4. Daniels, S.L. 1980. "Mechanisms Involved in Sorption of Microorganisms to Solid Surfaces" in Adsorption of Microorganisms to Surfaces Bitton and Marshall, Eds.
5. Hendricks, C.W. 1971. Increased recovery rate of salmonellae from stream bottom sediments versus surface waters. Appl. Microbial. 21: 379.
6. Van Donsel, D.J. and E.E. Geldreich. 1971. Relationships of Salmonella to fecal coliforms in bottom sediments. Water Res. 5 1079-1087.
7. Hendricks, C.W. 1971. Enteric bacterial metabolism of stream sediment eluates. Can. J. Microbial. 17: 551.
8. Gerba, C.P. and J.S. McLeod. 1976. Effect of Sediments on the survival of Escherichia coli in marine waters. Appl. Environ. Murobial. 32: 114.
9. Wood, E.J.F. 1965. Marine Microbial Ecology, Chapman and Hall Ltd., London, p. 24.
10. Gunnerson, C.G. 1963. Mineralization of organic matter in Santa Monica Bay, California in Symposium on Marine Microbiology, C.H. Oppenheimer Ed., Charles C. Thomas, Springfield Il., p. 641-653.
11. Geldreich, E.E. 1970. Applying bacteriological parameters to recreational water quality. J. Amer. Wat. Works Assoc. 62 (2): 113-120.
12. Wetzel, R.G. 1975. Limnology W.B. Saunders Co., Philadelphia, PA.
13. Avnimelech, Y., J.R. McHenry, and J.D. Ross. 1984. Decomposition of organic matter in lake sediments. Environ. Sei. and Technol. 18: 5-11.

14. Mitchell, R. and S. Yankofsky. 1969. Implication of a marine amoeba in the decline of Escherichia coli in seawater. Environ. See. Technol. 3: 574.
15. Brock, T.D. 1971. Microbial growth rates in nature. Bacterial. Revs. 35: 39.
16. Marshall, K.C. 1971. Sorptive interactions between soil particles and microorganisms in Soil Biochemistry Vol. II, A.D. McLaren and J.J. Skijens, Eds., Marcel Dekker, New York, p. 409-445.
17. Daniels, S.L. 1968. Separation of bacterial by adsorption onto ion exchange resins. Ph.D. Thesis, University of Michigan, Ann Arbor, Diss. Abstr. 29, 1336 B.
18. Berger, B.D., F.A. Butrico, H.J. Dunsmore, V.C. Lischer, H.F. Ludwig, F. Nevins, G.W. Reid, H. Romer and O.J. Sproul. 1970. Engineering Evaluation of Virus Hazards in Water. J. San. Eng. Div. 96: 111.
19. Matson, E.A., S.G. Hornor, and J.D. Buck. 1978. Pollution indicators and other microorganisms in river sediments. J. W.P.C.F. 39: R45-R63.
20. Erkenbrecher, C.W. Jr. 1980. Sediment bacteria as a water quality indicator in the Lynnhaven estuary. Virginia, U.S.A., VA Polytech Inst. State Univ. Water Resources Bull. 0 (126) I-X, 1-118.
21. Jenkins, A., M.J. Kirkly, A. McDonald, P. Waden, and D. Kay. 1984. Process based model of fecal bacterial levels in upland catchments. Water, Science and Tech. 16: 453-462.
22. Sayler, G.S. and C.M. Gilmour. 1978. Heteratrophic utilization of organic carbon in aquatic environments. J. Environ. Zual. 7 (3): 385-391.
23. Barnhart, C.L.H., and J.R. Vestal. 1983. Effects of Environmental Toxicants on Metabolic Activity of Natural Microbial Communities. Appl. and Environ. Microbiol. 46: 970-977.
24. Jameson, A.L.H. and J.R. Saxon. 1967. Field studies on the effect of daylight on mortality of coliform bacteria. Wat. Res. 1: 279-295.
25. Sjogren, R.E. and M.J. Gibson. 1981. Bacterial survival in a dilute environment. Appl. Environ. Microbial. 41: 1331-1336.
26. Hanes, N.B., G.A. Rohlich, and W.B. Sarles. 1966. The effect of temperature on the survival of indicator bacteria. New Eng. Wat. Works assoc. 80: 6-18.

27. McFeters, G.A. and D.G. Stuart. 1972. Survival of fecal coliform bacteria in natural waters. Field studies with membrane filter chambers. Appl. Microbiol. 24: 805-811.
28. Geldreich, E.G., C.C. Best, B.A. Kenner and D.J. Van Donsel. 1968. Bacteriological aspects of stormwater pollution. Journal WPFC. 40(11): 1861-1872.
29. McNeil, A.R. 1985. Microbial water quality criteria: a review for Australia. Australian Water Resources Council Technical Paper No. 85: 1-447.
30. Mundt, J.O. 1963. Occurrence of enterococci on plants in a wild environment. Appl. Microbiol 11: 141.
31. Geldreich, E.E. B.A. Kenner and P.W. Kabler. 1964. Occurrence of coliforms, fecal coliforms and streptococci on vegetation and insects. Appl. Microbiol. 12: 63.
32. Geldreich, E.E. and B.A. Kenner. 1969. Concepts of fecal streptococci in stream pollution. J. Water Pollution Control Fed. 41: R336-352.
33. Gartner, Lee and Associates. 1983. Humber River and tributary dry weather outfall study. Toronto Area Watershed Management Strategy Study Technical Report #1. Ontario Ministry of Environment.
34. Dutka, B.J. and K.K. Kwan. 1980. Bacterial die-off and stream transport studies. Wat Res. 14: 909-915.
35. Geldreich, E.E. 1976. Fecal Coliform and fecal streptococci density relationships in waste discharges and receiving waters. CRC Critical Reviews in Environmental Control. 6(4): 349-369.
36. Sjogren, R.E. and M.J. Gibson. 1981. Bacterial survival in a dilute environment. Appl. and Environ. Microbiol. 41(6): 1331-1336.
37. Kittrell, F.W. and S.A. Furfari. 1963. Observations of coliform bacteria in streams. J. Water Poll. Control Fed. 35: 11.
38. Strecker, H.W. 1934. A formulation of bacterial changes occurring in polluted water. Sew. Works. J. 6: 208.
39. Van Donsel, D.J., E.E. Geldreich and N.A. Clark. 1967. Seasonal variations in survival of indicator bacteria in soil and their contribution to stormwater pollution. Appl. Microbiol. 15: 1362-1370.
40. Evans, M.R. and J.D. Owens. 1972. Factors affecting the concentrations of fecal bacteria in land-drainage water. J. Gen. Microbiol. 71: 477-485.

FEASIBILITY OF PLANT HARVESTING IN WATER QUALITY AMELIORATION AND NUTRIENT MANAGEMENT IN SHALLOW IMPOUNDMENTS

K. Clarke-Whistler¹, P.M. McKee¹ and G. Gaspard²

¹Beak Consultants Limited, Mississauga, Ontario

²Credit Valley Conservation Authority, Mississauga, Ontario

ABSTRACT

In a survey of southern Ontario reservoirs, eutrophication, as indicated by aquatic weed proliferation and/or algal blooms, was reported as a major management problem in over 80% of the impoundments. Aquatic plant harvesting may be useful in nutrient management in the reservoirs. In shallow impoundments where macrophyte biomass is high relative to the total volume of water, long-term harvesting, combined with control of nutrient sources, may effectively reduce loadings to downstream waters.

The Orangeville Reservoir, located at the headwaters of the Credit River, is highly eutrophic and contains heavy growth of aquatic macrophytes (*Myriophyllum* spp.). The Credit Valley Conservation Authority wishes to maintain or improve water quality and to improve the recreational potential of the reservoir. To this end, a mechanical plant harvesting program was initiated in 1984. This study evaluates the harvesting program and its potential for water quality improvement in Orangeville Reservoir.

Based on an estimated input-output budget for phosphorus and nitrogen, the reservoir was found to act as a nutrient sink. The major storage compartment for both nitrogen and phosphorus was the highly organic sediments. Net phosphorus retention by aquatic vegetation was small; therefore, it is unlikely that plant harvesting will reduce phosphorus concentrations in the water. This was attributed to most of the phosphorus used by plants being obtained from the sediments. There was no indication of phosphorus release during winter die-off, suggesting that phosphorus tied up in the plants is returned to the sediments. On the other hand, up to 67% of total nitrogen requirements of plants appeared to be met from the water column. Thus, harvesting represents a potentially effective method of nitrogen control.

The monitoring program has been expanded and is being continued through one full year (1986) using more intensive water quality sampling and streamflow measurements to refine the nutrient budgets and to determine harvesting optimality in biomass and nutrient removal in the reservoir. The 1986 program will be complete in December 1986, and will be reported in early 1987.

INTRODUCTION

Over recent years, major initiatives to reduce nutrient loading to the Great Lakes have been made in Canada and the United States. However, recent reports from both the Pollution from Land Use Activities Reference Group (PLUARG) and the Great Lakes Water Quality Agreement Board indicate low cost, technologically simple measures such as phosphate reduction in household detergents and upgrading of municipal sewage treatment plants may not be stringent enough to achieve the water quality objectives for the lower Great Lakes as stated in the agreement. In addition, multi-year studies show that loadings of inorganic nitrogen compounds to the lower Great Lakes basin are increasing (Taub, 1984). Aquatic plant harvesting represents a simple and relatively low cost method of nutrient management which has received little attention to date. Generally, nutrient loss due to plant removal is insignificant compared to the total nutrient budget in a waterbody, especially in the sediments. However, in some situations where macrophyte biomass is high in relation to the total volume of water (e.g., in shallow ponds and impoundments), long-term harvesting, combined with control of nutrient sources, may remove a sufficient portion of nutrients to significantly improve water quality.

During the 1950's and 1960's, numerous shallow reservoirs and ponds were created by dam construction in southern Ontario river systems to provide flood control in the spring and streamflow augmentation during summer low flows. A recent survey of such reservoirs currently being managed by conservation authorities, was conducted by Credit Valley Conservation Authority. Fifty-one impoundments ranging from 3.6 to 2,000 hectares, were identified. The majority of these reservoirs are shallow (<5 m) water bodies. Over 80% of the survey responses reported eutrophication as a major reservoir management problem. Common eutrophication indicators were aquatic weed proliferation and/or algae blooms. Many respondents reported high surface coverage by aquatic weeds and phosphorus concentrations in excess of Ontario Ministry of the Environment (MOE) guidelines. Weed control methods are employed in 29 of the 51 reservoirs. The most common control method is a combination of winter drawdown and chemical spraying. Mechanical weed harvesting was used in four reservoirs and was under consideration for an additional five reservoirs.

The Orangeville Reservoir, located on the northeastern edge of the Town of Orangeville at the headwaters of the Credit River, is typical of many southern Ontario reservoirs. It is highly eutrophic and contains heavy growths of aquatic macrophytes (Myriophyllum spp.). In 1984, a mechanical plant harvesting program was initiated as a weed control measure. In this study the harvesting program is evaluated, and the

potential for water quality improvement at Orangeville Reservoir and in other similar impoundments in southern Ontario is discussed.

The specific objectives for monitoring weed harvesting in Orangeville Reservoir are:

- to permit site-specific assessment of potential improvements in water quality which might be expected as a result of weed harvesting; and
- to provide a preliminary mechanism for assessing the technical and economic feasibility of harvesting as a management tool for nutrient control in similar impoundments.

During 1984, a preliminary study was conducted to identify key components of the nutrient budget in Orangeville Reservoir. Major study components include:

- quantification of the nutrient budget through a steady-state input-output model;
- identification of major nutrient storage compartments within the reservoir; and
- evaluation of the effect of nutrient removal by plant harvesting.

METHODS

Study Area

The Orangeville Reservoir is located on the eastern edge of the Town of Orangeville, at the headwaters of the Credit River. It forms the major part of the 344 ha Orangeville Reservoir Conservation Area, operated by the Credit Valley Conservation Authority.

The reservoir is a multi-use facility, which provides:

- water storage for low flow augmentation to the Orangeville Water Pollution Control Plant, located 1.8 km downstream;
- a land and water-based recreational facility; and
- habitat for migratory waterfowl.

The reservoir was formed in 1967. Dykes were constructed at the north and south ends of the then existing cedar swamp to create an impoundment with a maximum

surface area of 173 ha. Flow control and overflow structures are located at the south dyke (Figure 1).

The reservoir drainage basin is 27.2 km². Four springfed streams, the largest being Monora Creek, flow into the reservoir and a fifth spring is located under it. Total water capacity is 3.08×10^6 m³. A volume of 1.57×10^6 m³ has typically been maintained for flow augmentation. Dam operation was originally scheduled to achieve a minimum year round flow of 0.28 m³/sec. However, the reservoir policy was modified in 1978 to facilitate water-based recreational activity and enhance waterfowl habitat. During the summer, the control valve is closed and high water levels are maintained. Flow to the Credit River occurs as seepage (about 0.014 to 0.057 m³/sec) through the dyke. During August through November, the valve is opened to allow higher flows for low flow augmentation. By the end of November, the reservoir is at its lowest level. It is maintained at this level through the winter to maximize storage capacity for the spring thaw (IEC, 1981).

The reservoir is shallow with extensive marshland. Open water areas are approximately 2.7 to 3.4 m deep. The average depth of the reservoir, including the marsh, is 1.5 m. A deep (7.6 m) hole occurs in the eastern arm (Figure 1). During the summer months, the entire surface of the reservoir is covered by extensive aquatic weed growth. The dominant species are Myriophyllum spp. (excalbescens and/or spicatum).

Sampling Methods and Analysis

Much of the data used in calculating nutrient budgets were obtained from the unpublished and published reports referenced in each section. However, a small number of samples were collected from the reservoir to verify historical data. Samples of water, macrophytes and sediments were collected during August 1984. An additional set of water samples were collected in October 1984. As shown in Figure 1, six sampling stations were located at various locations in and around the reservoir. These included shallow and deep locations, harvested and unharvested sites, inflows and the outflow. At each reservoir sampling station, vertical temperature, pH, conductivity and oxygen profiles were taken. Water samples were collected from 0.5 m below the surface and 0.5 m above the bottom using a Van Dorn sampler. During the August sampling period, a large (10 L) water sample was collected from each station in order to determine suspended particulate (seston) concentrations. Surface sediment samples (10 cm) were collected from each reservoir station by Ekman dredge. Triplicate vegetation samples (0.25 m²) were collected from each reservoir station by SCUBA diver. All above and below ground parts were collected.

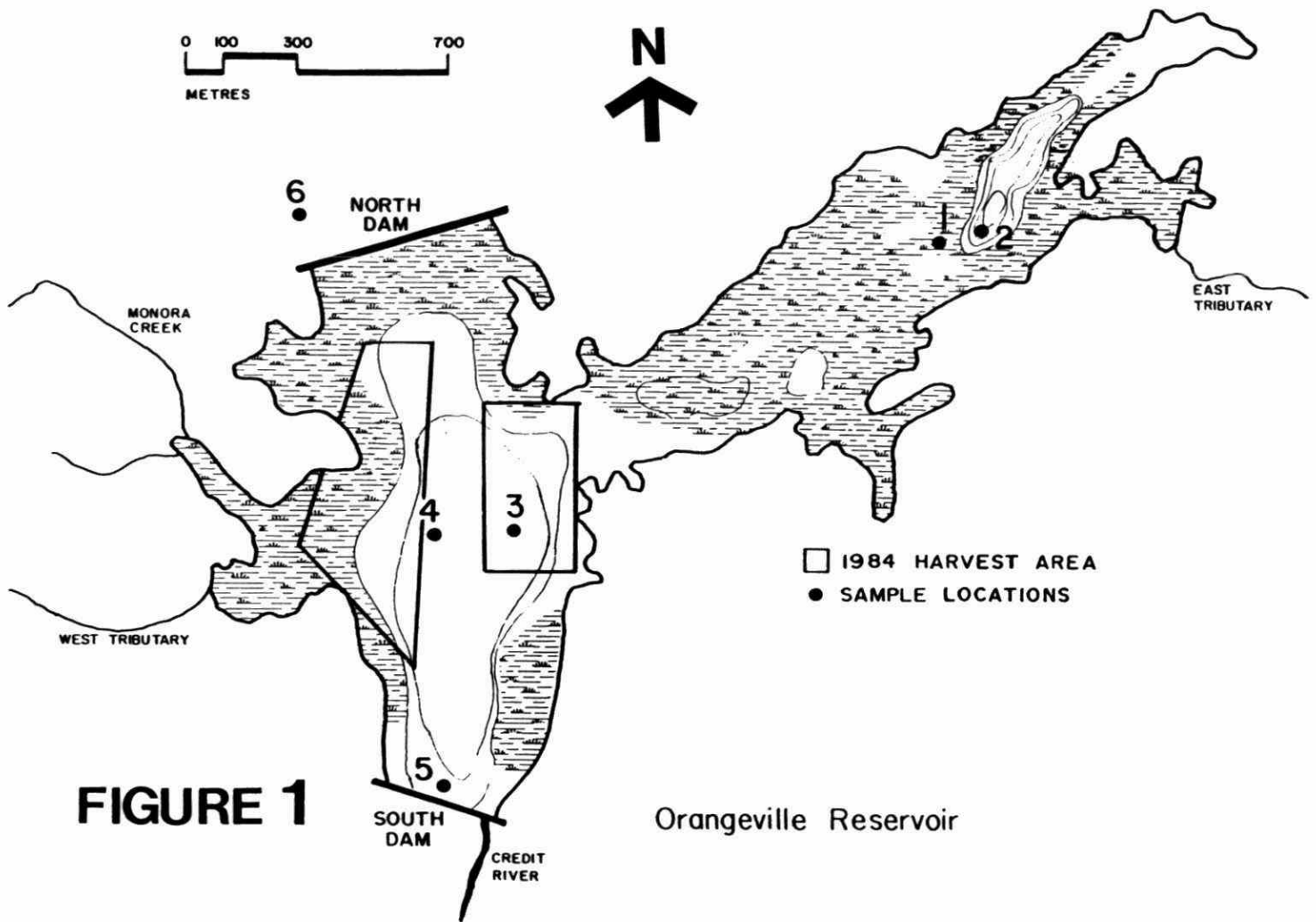


FIGURE 1

Nutrient analysis of water, vegetation and sediment samples were performed at the Laboratory Services Branch of the MOE. Analytical methods are outlined in the MOE Outlines of Analytical Methods (1975).

RESULTS

Calculation of Nutrient Budget

A preliminary nutrient budget for phosphorus and nitrogen was determined using a steady-state input-output model of the form:

$$\text{Nutrient Storage} = \text{Input} - \text{Output}$$

Input sources include atmospheric deposition and surface water inflow. Overland flow and groundwater are considered negligible given the small drainage area. Output is based on dam outflow. Losses via seepage are considered insignificant. Major components of the nutrient budget are discussed in the following sections.

Atmospheric Deposition

Annual loadings of total phosphorus (TP) and total nitrogen (TN) via precipitation and dry deposition were calculated according to the formula:

$$\begin{aligned} \text{Input atmospheric} &= (\text{nutrient precipitation} + \text{nutrient dry deposition}) \\ &\times \text{volume of precipitation} \times \text{surface area of reservoir} \end{aligned}$$

All loading calculations assume a reservoir surface area of $1.6 \times 10^6 \text{ m}^2$.

Precipitation inputs are summarized in Table 1. Seasonal average rainfall values are based on long-term averages recorded at the Orangeville MOE monitoring station (AES, 1982). Nutrient concentrations in precipitation are from the Acidic Precipitation in Ontario Study (APIOS) station at Palmerston, Ontario. This station is within 80 km of Orangeville and receives precipitation from similar sources. Concentration data are based on monthly samples collected over the fifteen month period from September 1980 - December 1981 (Chan *et al.*, 1983).

Dry deposition values for nitrogen are derived from isopleths of NO_3 deposition for southern Ontario (M. Lusic, unpublished). A value of $0.6 \text{ g/m}^2/\text{yr}$ was interpolated for the Orangeville area. This value is considered to more accurately represent total nitrogen deposition and is included as such in loading calculations (M. Lusic, pers. comm.).

TABLE 1: NUTRIENT INPUTS TO ORANGEVILLE RESERVOIR VIA ATMOSPHERIC DEPOSITION
(Reservoir surface area = $1.6 \times 10^6 \text{ m}^2$)

A. Wet Deposition

	Total Precipitation (mm)	Volume of Precipitation ($\times 10^3 \text{ m}^3$)	Nutrient Concentration (g/m^3)				Nutrient Loading (kg)			
			TP	TKN	NO_3	NH_4	TP	TKN	NO_3	NH_4
Spring	201.6	3.23	0.0171	1.211	0.787	1.055	5.52	390.6	254.4	340.3
Summer	231.8	3.71	0.0176	0.887	0.536	0.680	6.53	329.0	198.4	252.2
Fall	223.8	3.58	0.0270	0.901	0.501	0.672	9.67	322.6	179.2	240.6
Winter	185.6	2.97	0.0050	0.840	0.636	0.648	1.48	249.4	188.9	192.4
Total	842.8	13.49					23.20	1291.6	820.9	1025.5

B. Dry Deposition

$$\text{Total Phosphorus} = 0.0385 \text{ g/m}^2/\text{yr} \times 1.6 \times 10^6 \text{ m}^2 = 61.6 \text{ kg}$$

$$\text{Total Nitrogen (as } \text{NO}_3) = 0.6 \text{ g/m}^2/\text{yr} \times 1.6 \times 10^6 \text{ m}^2 = 960 \text{ kg}$$

C. Total Nutrient Loading

$$\begin{aligned} \text{Total Phosphorus} &= (\text{Total Phosphorus})_{\text{wet}} + (\text{Total Phosphorus})_{\text{dry}} \\ &= 23.20 + 61.60 \\ &= 85 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Total Nitrogen} &= (\text{Total TKN} + \text{Total } \text{NO}_3)_{\text{wet}} + (\text{Total Nitrogen})_{\text{dry}} \\ &= 1291.6 + 820.9 + 960 \\ &= 3070 \text{ kg} \end{aligned}$$

Phosphorus deposition was back-calculated and extrapolated from a long-term bulk depositional value of $35 \text{ mg/m}^2/\text{yr}$ TP, measured for the Muskoka-Haliburton area (P. Dillon, pers. comm). Bulk nutrient deposition would be expected to be significantly higher than this value in an agricultural area such as that surrounding Orangeville. Based on comparison with nitrogen deposition isopleths, a total of $53 \text{ mg/m}^2/\text{yr}$ TP was assumed to be appropriate for Orangeville. By subtracting the calculated TP deposition via precipitation ($14.5 \text{ mg/m}^2/\text{yr}$), a value of $38.5 \text{ mg/m}^2/\text{yr}$ TP was derived for dry deposition.

Based on the above calculations, summarized in Table 1, totals of 3,070 kg of nitrogen and 85 kg of phosphorus annually are estimated to enter the Orangeville Reservoir via atmospheric deposition.

Surface Inflow

Surface inflow is calculated as:

$$\text{Surface Inflow} = \text{volume inflow} \times \text{nutrient concentration}$$
$$(\times 10^5 \text{ m}^3) \quad (\text{g/m}^3)$$

As shown in Figure 1, surface inflow to Orangeville Reservoir is via four small springfed streams. During August 1984, stream inflow was monitored by CVCA for a two week period, and an average daily discharge value of $0.0830 \text{ m}^3/\text{sec}$ was derived. Streamflow data for the remainder of the year were extrapolated from monitored streams which displayed similar discharge or water quality characteristics (Tables 2 and 3). Composite nutrient samples were collected during the same time period.

Stream discharge was calibrated against the Schomberg River (Water Survey of Canada, 1983; Station Number O23COAO). This small stream has a drainage area of 42.9 km^2 and a basin comprised primarily of farmland. Flow characteristics and inflow calculations are shown in Table 2.

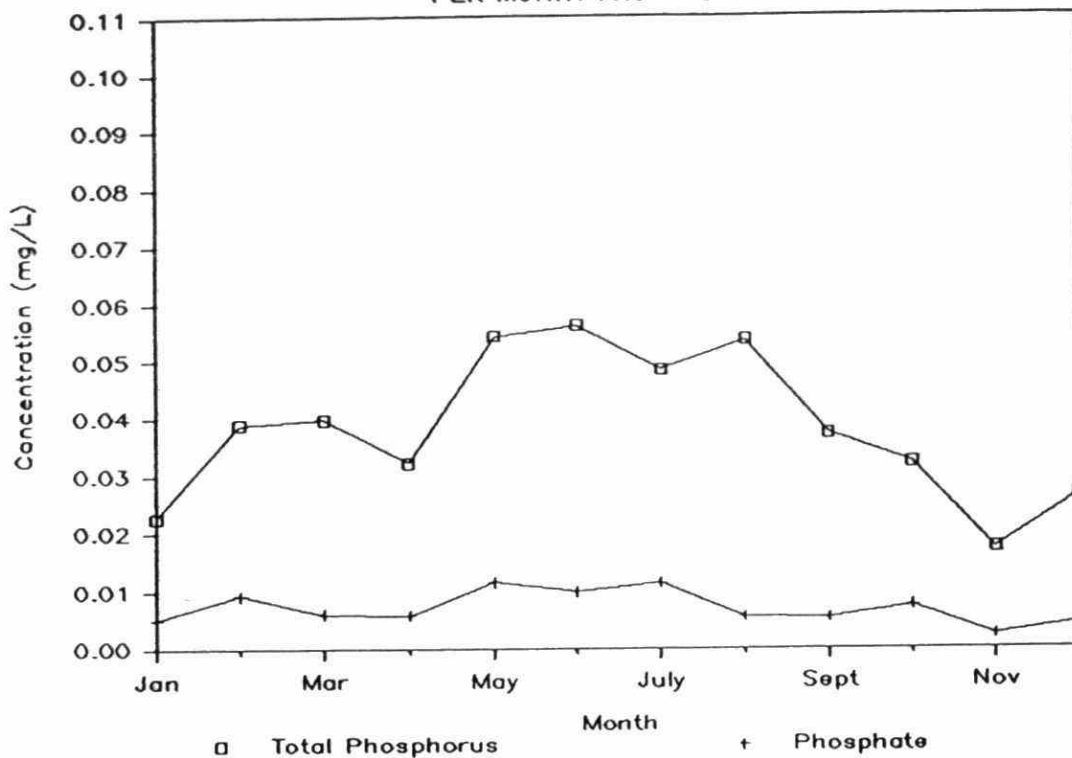
Nutrient samples were collected at Monora Creek in August and October. Data for the remainder of the year were extrapolated from average concentrations in the Orangeville Reservoir outflow (Table 3; Figure 2). August and October inflow concentrations are within the 95% confidence interval of mean outflow concentrations. Based on these calculations the total nutrient input to the reservoir via inflow is $1.46 \times 10^4 \text{ kg}$ TN and 433 kg TP.

FIGURE 2

NUTRIENT CONCENTRATIONS IN ORANGEVILLE RESERVOIR OUTFLOW

AVERAGE PHOSPHORUS CONCENTRATION

PER MONTH FROM 1977-84



AVERAGE NITROGEN CONCENTRATION

PER MONTH FOR 1977-84

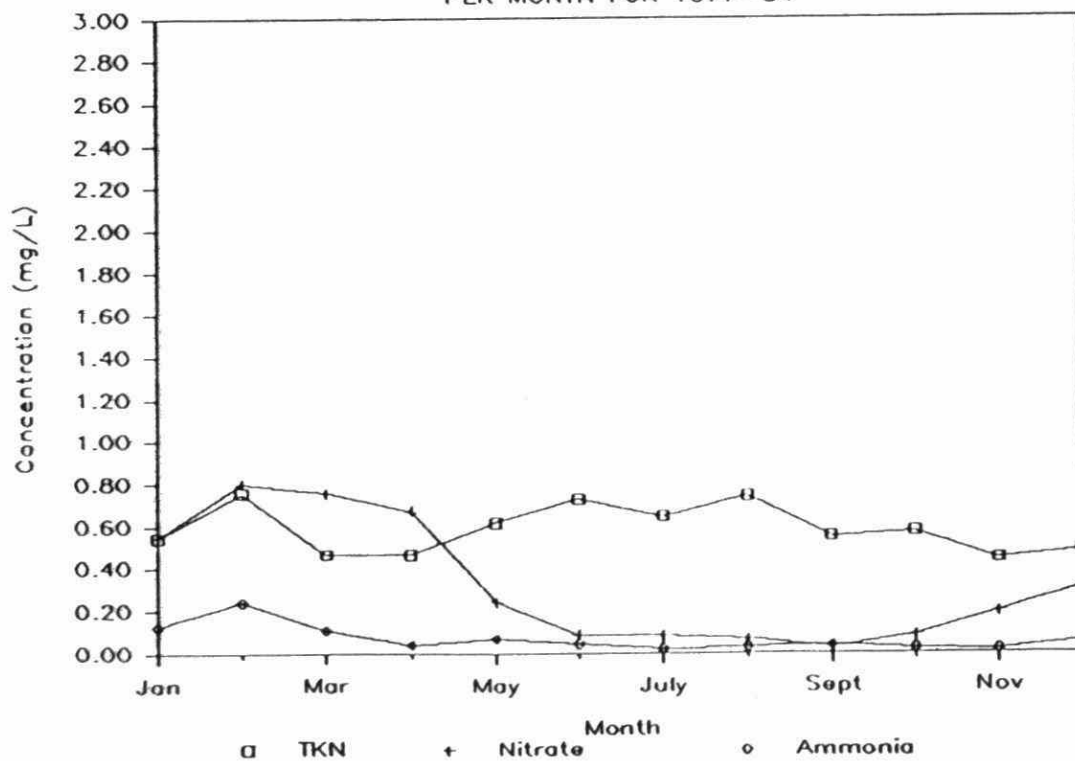


TABLE 2: DERIVATION OF NUTRIENT INPUTS TO ORANGEVILLE RESERVOIR VIA SURFACE INFLOW

A. Discharge Data for Schomberg River

Month	Mean Daily Discharge (cms)	Monthly Volume ($\times 10^5 \text{ m}^3$)	Calculated Inflow to Orangeville Reservoir ($\times 10^5 \text{ m}^3$)
January	0.228	6.11	7.14
February	0.326	7.89	9.22
March	0.999	26.75	36.18
April	0.815	21.12	28.52
May	0.238	6.37	7.45
June	0.115	2.98	3.48
July	0.100	2.68	3.13
August	0.071 (0.083*)	1.90	2.57*
September	0.077	2.00	2.34
October	0.146	3.91	4.57
November	0.213	3.52	4.11
December	0.270	<u>7.23</u>	<u>8.45</u>
		49.38	58.06

B. Nutrient Load To Orangeville Reservoir Via Inflow (kg)

	TP	TKN	NO ₃ **
January	16.4	387.7	389.1
February	36.0	697.0	739.4
March	144.7	1,689.6	4,652.7
April	91.3	1,326.2	1,908.0
May	40.2	458.2	180.3
June	19.5	252.3	30.3
July	15.0	200.6	26.3
August	13.9	190.7	17.7
September	8.7	128.7	7.0
October	14.6	260.9	6.9
November	7.0	180.8	80.1
December	<u>22.8</u>	<u>410.7</u>	<u>262.8</u>
	430	6,183.5	8,300.8

* = Orangeville Reservoir

** = NO₃ + NO₂

Annual Nutrient Load via Inflow:

Total Phosphorus = 430 kg
 Total Nitrogen = 1.45×10^4 kg

TABLE 3: ANNUAL NUTRIENT LOADING TO THE CREDIT RIVER VIA OUTFLOW FROM ORANGEVILLE RESERVOIR

	Mean Daily Discharge (cms)	Monthly Volume (x 10 ⁵ m ³)	Mean Nutrient Concentration (1977- 1984) (g/m ³)			Nutrient Loading (kg)		
			TP	TKN	NO ₃ *	TP	TKN	NO ₃ *
January	0.318	8.52	0.023	0.543	0.545	19.60	462.6	464.7
February	0.242	5.85	0.039	0.756	0.802	22.82	442.3	469.0
March	0.205	5.49	0.040	0.467	1.286	21.96	256.4	706.1
April	0.227	5.88	0.032	0.465	0.669	18.82	273.4	393.3
May	0.698	18.70	0.054	0.615	0.242	100.98	1150.1	451.6
June	0.211	5.47	0.056	0.725	0.087	30.63	396.6	47.6
July	0.208	5.57	0.048	0.641	0.084	26.74	357.0	47.0
August	0.220	5.89	0.054	0.742	0.069	31.81	437.0	40.4
September	0.214	5.55	0.037	0.550	0.030	20.54	305.3	16.7
October	0.205	5.49	0.032	0.571	0.015	17.57	313.5	8.0
November	0.288	7.46	0.017	0.443	0.195	12.68	330.5	145.8
December	0.284	7.61	0.027	0.486	0.311	20.55	369.8	236.3
			\bar{x} 0.038	\bar{x} 0.584	\bar{x} 0.361			

Annual Loading via Outflow:

345 5,094 3,026

Total Phosphorus = 344.7 kg

Total Nitrogen = 8,120.9 kg

* = NO₃ + NO₂

Outflow

Surface outflow was calculated from monthly means of historical discharge and water quality data collected at the reservoir outflow dam (Table 3; Figure 2). Outflow was calculated as:

$$\text{Surface Outflow} = \text{volume outflow} \times \text{nutrient concentration}$$

$$(\times 10^5 \text{ m}^3) \quad (\text{g/m}^3)$$

Since the dam outflow is regulated, discharge does not follow typical seasonal patterns associated with spring melt. Maximum outflow occurs in May, approximately two months after the major spring runoff, and winter discharge values are higher than might normally be expected as a result of low flow augmentation.

Average monthly nutrient concentrations are shown in Figure 2. Average monthly total phosphorus concentrations range between 0.017 and 0.056 mg/L, with an annual average of 0.038 mg/L. Maximum concentrations generally occur during summer. Bioavailable phosphate averages less than 0.010 mg/L and shows little annual variation.

TKN concentrations show a similar seasonal pattern similar to that of TP concentrations, averaging 0.584 mg/L over the year. The bioavailable forms of nitrogen, nitrate and ammonia, show seasonal patterns associated with uptake and release by biota. Concentrations of both forms are lowest during the spring and summer months, when primary and secondary production is high. High concentrations during the fall and winter months (up to 1.286 mg/L) may be attributable to releases resulting from plant die-off and incorporation into the anaerobic sediments.

Based on the data in Table 3, annual nutrient loadings to the Credit River via outflow from the Orangeville Reservoir are calculated as 345 kg total phosphorus and 8120 kg total nitrogen.

Nutrient Budget

Based on the calculations in the preceding sections, the nutrient budget for Orangeville Reservoir is:

$$\begin{aligned} \text{Reservoir Storage of Total Phosphorus} &= \text{TP}_{\text{input}} - \text{TP}_{\text{output}} \\ &= 85 \text{ kg} + 430 \text{ kg} - 345 \text{ kg} \\ &\quad (\text{atmos}) \quad (\text{inflow}) \quad (\text{outflow}) \\ &= 170 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Reservoir Storage of Total Nitrogen} &= 3,070 \text{ kg} + 1.45 \times 10^4 \text{ kg} - 8,120 \text{ kg} \\ &\quad (\text{atmos}) \quad (\text{inflow}) \quad (\text{outflow}) \\ &= 9,450 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Reservoir Storage of Nitrate} &= 1,780 \text{ kg} + 8,300 - 3,026 \\ &\quad (\text{atmos}) \quad (\text{inflow}) \quad (\text{outflow}) \\ &= 7,054 \text{ kg} \end{aligned}$$

In light of the simplified nitrogen cycle used and the inaccuracy of measurement associated with inflow and atmospheric deposition, errors of 20 to 30% may be associated with these budgets. Nonetheless, on an annual basis the reservoir appears to act as a nutrient sink, rather than a source. The calculated budgets indicate that approximately 33% of the net annual total phosphorus input and 55% of the total nitrogen input are retained.

Nutrient Storage

The effectiveness of plant harvesting as a means of water quality improvement depends on the total nutrient load removed from the water by macrophytes. As indicated in the previous sections, a significant proportion of the nitrogen and possibly some of the phosphorus entering the reservoir is retained. Nutrient storage compartments within the reservoir include aquatic macrophytes, sediments and the water column. Fish and aquatic macroinvertebrates are considered negligible. The relative importance of the major storage compartments are discussed in the following sections.

Macrophytes

The total biomass of macrophytes, including above and below ground parts is calculated in Table 4. Total biomass in shallow waters (<2.5 m) ranges between approximately 920 and 2,700 g/m². Biomass was significantly lower in samples collected at depths of 5 m, confirming reports of maximum Myriophyllum productivity at depths of less than 4 m (Grace and Tilly, 1976). In calculating total standing crop, it was assumed that 5% of the reservoir bottom is greater than 5 m deep (Figure 2), and that Myriophyllum bottom coverage was 50% (Table 4). Thus a total biomass of 5.02×10^5 kg dry weight was derived. Average nutrient concentrations in macrophytes were 0.21% and 2.09% for total phosphorus and total nitrogen, respectively. Thus the aquatic vegetation contains an estimated total of 1,053 kg of phosphorus and 1.05×10^4 kg of nitrogen (Table 4).

TABLE 4: TOTAL NUTRIENT CONTENT OF AQUATIC MACROPHYTES IN ORANGEVILLE RESERVOIR

Location	Depth (m)	Biomass (g/m ² dry weight)	Total Nitrogen (%)	Total Phosphorus (%)
<u>Station 1</u>	1.2			
		921.8	1.89	0.12
Replicate - 1		1,768.2	1.77	0.12
- 2		<u>1,410.0</u>	<u>1.72</u>	<u>0.10</u>
- 3		\bar{x} Total = 1,366.7	\bar{x} = 1.79	\bar{x} = 0.11
		\bar{x} Above-ground = 820.0		
<u>Station 2</u>	5			
		6.2	2.85	0.22
Replicate - 1		12.2	3.26	0.41
- 2		<u>4.2</u>	<u>3.00</u>	<u>0.26</u>
- 3		\bar{x} Total = 7.5	\bar{x} = 3.04	\bar{x} = 0.30
		\bar{x} Above-ground = 4.5		
<u>Station 3</u>	2.1 (cutover)			
		284.0	1.83	0.19
Replicate - 1		180.0	1.93	0.20
- 2		<u>168.0</u>	<u>1.40</u>	<u>0.15</u>
- 3		\bar{x} Total = 210.7	\bar{x} = 1.72	\bar{x} = 0.18
		\bar{x} Above-ground = 126.4		
<u>Station 4</u>	2.1			
		2,660.0	1.41	0.18
Replicate - 1		1,960.0	1.91	0.27
- 2		<u>1,180.0</u>	<u>2.12</u>	<u>0.29</u>
- 3		\bar{x} Total = 1,933.0	\bar{x} = 1.81	\bar{x} = 0.25
		\bar{x} Above-ground = 1,160.0		

Average above-ground biomass for non-cutover areas = $(820.0 + 1,160.0) \times 95\% + (4.5) 5\%$
 (weighted by depth) = 627.1 g/m² dry weight

Total biomass assuming 50% bottom coverage = 5.02×10^5 kg
 (bottom area = 1.6×10^6 m²)

Total Phosphorus = 1,053 kg
 Total Nitrogen = 1.05×10^4 kg

Sediment

Surface (10 cm) sediments are highly organic and largely composed of decaying Myriophyllum. Dry bulk densities are low (2.00 g/cm^3) reflecting the predominance of the organic material. Average nutrient contents in the top 10 cm were 0.13% and 1.56% for total phosphorus and total nitrogen, respectively. Based on these concentrations, and the sediment bulk density, a total of $4.2 \times 10^4 \text{ kg}$ total phosphorus and $5.0 \times 10^5 \text{ kg}$ total nitrogen are contained in the surface sediments. Sedimentation rates would need to be measured to determine annual sedimentary loss of nutrients.

Water

Nutrient contents in unfiltered water samples collected during this study fall within historical ranges reported for the reservoir outflow. In calculating nutrient storage in the water column, historical water quality data collected at the reservoir outflow between 1977 and 1984 were used. The average TP concentration in the reservoir, over these eight years, was 0.038 mg/L , whereas the average TN concentration was 0.945 mg/L . The total water volume in the reservoir, based on a surface area of $1.6 \times 10^6 \text{ m}^2$, is $1.24 \times 10^6 \text{ m}^3$ (1,939 acre-feet) (M.M. Dillon Ltd., 1966). Thus the total nutrient content of the water column is 47 kg TP and 1,170 kg TN.

Suspended particulate concentrations in the outflow typically range between 1 and 15 mg/L. However, sampling conducted during this study indicated that wind turbulence resulted in higher particulate levels within the reservoir. Particulate concentrations in samples collected in August and October, 1984, averaged approximately 25 mg/L. Comparisons between nutrient concentrations of filtered and unfiltered waters indicated that 28% of TP and 25% TN was associated with suspended particulates. Therefore, a total nutrient load of 1.3 kg TP and 293 kg TN is associated with the suspended solids and the remainder (45.7 kg and 879 kg, respectively) is contained in dissolved forms.

Biomass Removal by Plant Harvesting

Weed harvesting began in late July, 1984 and continued, five days per week until 25 September. Total cutting time was 178 hours. Because 1984 was the first year of weed cutting, the working season was short and harvesting efficiency was low. Productivity rates are expected to increase substantially during subsequent harvesting seasons as operators gain better understanding of the system.

The total biomass removed via harvesting was calculated based on the number of harvester loads times the average load weight (1,000 lbs) (Table 5). Thus an estimated total biomass of 2.13×10^5 kg wet weight was removed. This is equivalent to 1.85×10^4 kg dry matter, based on an average moisture content of 91.3% obtained in the calculation of the total reservoir biomass. Assuming TP and TN content of 0.21% and 2.09% respectively, a total of 39 kg TP and 390 kg TN were removed via plant harvesting. These loads represent approximately 3.7% of the total nutrients contained in the aquatic vegetation.

The total plant biomass which might ultimately be removed from the reservoir once harvesting efficiency has been optimized may be roughly estimated from results of a similar harvesting operation conducted in Lake Chemung, Ontario. An overall seasonal average cutting rate of 0.15 ha/hour was achieved (Wile and Hitchin, 1977). Based on a seasonal estimate of 400 to 500 hours of cutting time for the Orangeville Reservoir operation (G. Gesparidy, Pers. Comm.), a total of 60 to 75 ha per season could be cut. This is roughly equivalent to a complete cutting of the western arm of the Orangeville Reservoir. Harvesting removes approximately 80% of the above-ground biomass (Table 4). If it is assumed that the western arm of the reservoir contains 50% of the total biomass, then harvesting would remove a total of 2.01×10^5 kg dry weight of biomass, or 420 kg TP and 4,200 kg TN. These weights are equivalent to 40% of the nutrients contained in the aquatic vegetation.

DISCUSSION

In assessing the feasibility of mechanical weed harvesting as a method of nutrient management it is necessary to determine both the efficiency of biomass removal and the net removal of nutrients by the vegetation. Harvesting efficiency depends on biomass, regrowth rates and methods of reproduction of the dominant plant species. In determining the potential for improvement in water quality, it is necessary to identify the major nutrient sources to the vegetation and the potential for release of nutrients by the vegetation after die-off.

Harvesting Efficiency

Historical records of the effects of mechanical harvesting on water milfoil have produced conflicting results. Mechanical harvesting of Eurasian water milfoil from Chemung Lake in Ontario were shown to reduce stem densities (Wile and Hitchin, 1977). Similarly, Bryant (1970) demonstrated that Eurasian water milfoil regrowth was retarded after harvesting. Research on American water milfoil, likewise indicated an initial

TABLE 5: BIOMASS REMOVED VIA MECHANICAL PLANT HARVESTING
DURING 1984

Total biomass = Number of harvester loads x wet weight x moisture content

$$= 470 \text{ loads} \times 1,000 \frac{\text{lbs}}{\text{load}} \times 91.30\% \text{ moisture}$$

$$= 1.85 \times 10^4 \text{ kg}$$

Total P removed = $1.85 \times 10^4 \text{ kg} \times 0.21\% \text{ P}$

$$= 39 \text{ kg}$$

Total N removed = $1.85 \times 10^4 \text{ kg} \times 2.09\% \text{ N}$

$$= 390 \text{ kg}$$

reduction in density and a reduced rate of regrowth (less than 20 cm per month) (Seinwill, 1968). In multi-year studies, Kimbel and Carpenter (1979) found that even one harvest per year reduced Eurasian water milfoil production the following year. Most authors do agree, however, that more than one harvest per season is needed to control water milfoil regrowth (i.e., Nichols, 1974; Wile and Hitchin, 1977). Kimbel and Carpenter (1979) found multiple harvests to be more effective than single harvests in reducing the amount of regrowth within a growing season and that recovery from a single harvest declines as the date of harvesting becomes progressively later in the season. This pattern correlates with declining water milfoil productivity in the late summer and early fall (Forsberg, 1959; Adams and McCracken, 1974). On the other hand, research in British Columbia (Anon, 1981) indicated that harvesting may actually stimulate water milfoil growth by removing the shading plant canopy, allowing greater light penetration to the basal shoots.

Results of the 1984 Orangeville cutting operation are too preliminary to draw meaningful conclusions. However, it should be noted that a single cutting reduced biomass in cutover areas by an average of 80%.

Water Quality Improvement

The use of mechanical harvesting to control nutrient concentrations in water has been shown to be effective for certain plant species such as water hyacinth which obtain nutrients largely from the water column (Steward, 1970; Sheffield, 1967). However, in general, the application of this technique to Eurasian water milfoil has not been effective in reducing the nutrient content of a water body unless concentrations are very high, e.g., 0.5 ug/mL (Bole and Allan, 1978).

Studies on nutrient uptake in both water milfoil species have generally indicated similar uptake patterns. Roots, as well as shoots, are capable of taking up and translocating nitrogen, phosphorus, and other nutrients in significant amounts. The ability of water milfoil to take up essential nutrients from whichever source is most available, is a significant ecological advantage.

While lakes exhibiting dense growths of Myriophyllum spicatum usually have water-borne phosphorus levels in excess of 0.02 mg/L (Forsberg, 1964), studies have indicated that when water milfoil is rooted, as is the case in the Orangeville Reservoir, phosphorus nutrition is independent of water concentration (Wilson, 1972; Bole and Allan, 1978). Root uptake of phosphorus (Mulligan and Baranowski, 1969; Bristow, 1975) has also been demonstrated in American water milfoil.

Based on the results of the nutrient input-output budget for Orangeville Reservoir, it appears that little phosphorus is removed from the water column by plant

uptake. Organic muck bottom sediments such as those found in the reservoir have been shown to provide an ideal nutrient source for both American and Eurasian water milfoil (Sculthorpe, 1967). While average total phosphorus concentrations in the water column are relatively high in the Orangeville Reservoir (up to 0.056 mg/L), phosphate phosphorus concentrations are significantly lower, accounting for only 14% of the total phosphorus loading on an annual basis (Figure 2). Thus, under these conditions the sediments represent a more favourable nutrient source.

The potential for nitrogen control through plant removal appears significantly higher. Based on the input-output budget, approximately 53% or 9,500 kg of the TN entering the reservoir is retained. Of this amount approximately 7,000 kg is in the form of nitrate. According to biomass calculations, the nitrate retained by the reservoir could account for approximately 67% of the TN contained in the plants. The importance of this mechanism of plant uptake is corroborated by the depletion of nitrate and ammonia from the water column during the growing season, despite the fact that atmospheric and inflow loadings are highest during this period of the year. Aquatic macrophytes also appear to introduce significant quantities of nitrogen into the water column through die-off, as indicated by increasing concentrations of inorganic nitrogen forms in the reservoir outflow during the fall and winter. Outflow loading data indicate that approximately 2,400 kg, or 80% of the total nitrate load from the reservoir to the Credit River occurs between November and April.

Nitrogen is recognized as a significant contributor to eutrophication in the upper Credit River. Based on an assimilative capacity study, the MOE (1980) suggests that nitrogen is the limiting nutrient in the system. The Town of Orangeville has similarly recognized nitrogen as a detriment to water quality in the upper Credit River, and has incorporated a denitrification unit into the expansion design of the Water Pollution Control Plant (WPCP).

In the environmental assessment for the WPCP expansion, IEC BEAK (IEC, 1981) calculated that nitrogen loadings from the Orangeville Reservoir and the WPCP accounted for 85-90% of the total nitrogen loading to the Credit River, measured at the Highway 10 crossing. Approximately 20% of the total loading was directly attributed to Orangeville Reservoir outflow. With the commencement of operation of the denitrification unit in the spring of 1985, it is anticipated that 85% of the nitrogen in the WPCP effluent will be removed. It has been calculated in this report that approximately 50% of the nitrogen in the Reservoir outflow could be permanently removed via plant harvesting. Thus the total nitrogen loading to the Upper Credit from these two sources could potentially be reduced by up to 65%.

An improvement in the dissolved oxygen regime of the reservoir may also be achieved as a result of harvesting. Fisheries studies conducted in the reservoir attribute critical oxygen deficiencies observed in both late summer and winter, to plant growth (nocturnal oxygen demand) and winter die-off (oxidation), respectively (McCartney and Fullard, 1973; McCartney, 1974; Hogg, 1975).

CONCLUSIONS AND RECOMMENDATIONS

It is recognized that the results of this study may be subject to large errors as a result of assumptions and inadequate data. Nonetheless, a number of interesting points are raised which might have practical implications for reservoir management in southern Ontario. Based on a simplified input-output budget for total phosphorus and total nitrogen, the Orangeville Reservoir was found to act as a nutrient sink rather than a source to downstream waters. The major storage compartment for both nitrogen and phosphorus is the highly organic sediments. However, aquatic vegetation contains significant amounts of potentially bioavailable nutrients. Net phosphorus retention by aquatic vegetation was small, and it is unlikely that plant harvesting will significantly improve phosphorus concentrations in the water. This condition is attributed to the fact that most of the phosphorus used by plants is obtained via the sediments. There is no indication of phosphorus release during winter die-off, suggesting that phosphorus tied up in the plants is returned to the sediments, thus completing the internal cycle.

On the other hand, about 67% of total nitrogen requirements by plants may be obtained from the water column. Thus harvesting represents a potentially effective method of nitrogen control. The need for nitrogen control in the upper Credit River has been recognized by both MOE and the Town of Orangeville in the incorporation of a denitrification unit in the Orangeville Water Pollution Control Plant.

Based on these conclusions it is recommended that the monitoring program be expanded and continued through at least one full growing season. This monitoring should include more extensive measurements of nutrient inputs. This recommendations was accepted by the Research Advisory Council of the MOE. One year of nutrient input and output measurements are being carried out on the Orangeville Reservoir in 1986.

REFERENCES

- Adams, M.S. and M.D. McCracken. 1974. Seasonal production of the Myriophyllum component of the littoral zone of Lake Wingra, Wisconsin. J. Ecol. 62:457-465.

- Anon. 1981. A summary of biological research on Eurasian milfoil in British Columbia. Vol. XI: Inf. Bull. Aquat. Plant. Manage. Program, B.C. Ministry of the Environment.
- Atmospheric Environment Service (AES). 1982. Canadian Climate Normals. Vol. 3: Precipitation 1951-1980. Environment Canada, 602 p.
- Bole, J.B. and J.R. Allan. 1978. Uptake of phosphorus from sediment or by aquatic plants, Myriophyllum spicatum and Hydrilla verticillata. Water Res. 12:353-358.
- Bristow, J.M. 1975. The structure and function of roots in aquatic vascular plants, pp. 221-236. IN: J.G. Torrey and D. Clarkson (eds.), The Development and Function of Roots. Acad. Press, N.Y.
- Bryant, C.B. 1970. Aquatic weed harvesting - Effects and Costs. Hyacinth Control J. 8(2):37-39.
- Chan, W.H., A.T.J.S. Tang and M.A. Lusi. 1983. Precipitation concentration and wet deposition fields of pollutants in Ontario, September 1980 to December 1981. Air Resources Branch, Ontario Ministry of the Environment, 79 p.
- Forsberg, C. 1964. The vegetation changes in Lake Takern, Sweden. Bot. Tidsk. 58:44-54.
- Forsberg, C. 1959. Quantitative sampling of subaquatic vegetation Crikos 10:233-240.
- Grace, J.B. and L.J. Tilly. 1976. Distribution and abundance of submerged macrophytes, including Myriophyllum spicatum in a reactor cooling reservoir. Arch. Hydrobiol. 77:475-487.
- Hogg, D.M. 1975. Orangeville Reservoir Creek Census. OMNR, 7 p.
- IEC Consultants Ltd. (IEC). 1981. Environmental Assessment Report for Water Pollution Control Plant Expansion. Town of Orangeville.

- Kimbel, J.C. and S.R. Carpenter. 1979. The dynamics of Myriophyllum spicatum biomass following harvesting. IN: J.E. Breck, R.T. Prentki and O.L. Loucks (eds.) Aquatic Plants, Lake Management and Ecosystem Consequences of Lake harvesting. Inst. Enviro. Studies. Univ. Wisconsin.
- M.M. Dillon Ltd. 1966. Orangeville Dam Project: Preliminary Engineering Report. Prepared for the Credit Valley Conservation Authority, 32 p.
- McCartney, M.J. 1974. Sex and the single trout or spawning beds at Orangeville Reservoir for speckled and rainbow trout. Prepared for the Credit Valley Conservation Authority, 4 p.
- McCartney, M.J. and J.H. Fulland. 1973. The Orangeville Reservoir: An Ecological Study. Prepared for the Credit Valley Conservation Authority, 168 p.
- Mulligan, H.F. and A. Baranowski. 1969. Growth of phytoplankton and vascular aquatic plants at different nutrient levels. Verh. Int. Ver. Limnol. 17:802-810.
- Nichols, S.A. 1974. Mechanical and Habitat Manipulation for Aquatic Plant Management. Wisconsin Dept. Nat. Res. Tech. Bull. No. 77, Madison, Wisconsin, 34 p.
- Ontario Ministry of the Environment (MOE). 1975. Outlines of Analytical Methods. Laboratory Services Branch, Technical Report, 94 p.
- Sculthorpe, C.D. 1967. The Biology of Aquatic Vascular Plants. Edward Arnold, London, 610 p.
- Seinwill, G.D. 1968. Mechanical Harvesting of Lake Weeds. Univ. Industry Res. Newsl., Univ. of Wisconsin, 3(3):16-17.
- Sheffield, D. 1967. IN: D.S. Mitchell (ed.). 1974. Aquatic vegetation and its use and control, UNESCO, Paris.
- Steward, K.K. 1970. Nutrient removal potentials of various aquatic plants. Hyacinth Control J. 8(2):34-35.

- Taub, F.B. (ed.) 1984. Lakes and Reservoirs. Ecosystems of the World, No. 23. Elsevier, Amsterdam, 643 p.
- Water Survey of Canada. 1983. Historical Streamflow Summary. Ontario - to 1982. Inland Waters Directorate, Environment Canada, Ottawa, 520 p.
- Wile, I. and G. Hitchin. 1977. An Assessment of the Practical and Environmental Implications of Mechanical Harvesting of Aquatic Vegetation in Southern Chemung Lake. Ontario Ministry of the Environment and Ministry of Natural Resources, 180 p.
- Wilson, D.O. 1972. Phosphate nutrition of the aquatic angiosperm, Myriophyllum excalbescens. Limnol. and Oceangr. 17(4).

TWO BIOASSAYS FOR THE RAPID DETERMINATION OF THE
EFFECTS OF DREDGED MATERIAL DISPOSAL ON PRIMARY
PRODUCTION AND PHOSPHORUS KINETICS IN OPEN
WATERS.

Calum N. Ewing and C. Nalewajko

Life Sciences Division, Scarborough Campus,
University of Toronto, Toronto, Ontario, M1C 1A4.

ABSTRACT:

The open water disposal of dredged lake sediments can have potential toxic effects on the primary production in the receiving waters. In addition, the availability of nutrients and their cycling can be greatly affected. To date studies of dredgeate toxicity have examined only the effects on photosynthesis and have used only the sediment elutriates to assess toxicity. We now present two bioassays that (1) allow the determination of toxic effects of whole sediments on primary production, as opposed to sediment elutriates or extracts, and (2) allow determination of the effects of whole sediments and elutriates on phosphorus cycling.

The effects of Lake Ontario sediments on the primary production and phosphorus kinetics of epilimnetic phytoplankton assemblages were investigated. Sediment toxicity was assessed using sediment elutriates and whole sediments. The effects of both, on primary production, were measured using the incorporation of ^{14}C , into DMSO extractable compounds, over a range of irradiances. Elutriates prepared from polluted sediments (Toronto Harbour) showed only minor toxic effects (24% depression of P_{max}) at a 10% (v/v) dosage. Whole sediment depressed the maximal photosynthetic rate (P_{max}) by up to 80%.

The effects of sediment disposal on phosphorus cycling were assessed using $^{32}\text{P-PO}_4$ uptake kinetics. Phosphate turnover time was found to increase with elutriate addition. The addition of whole sediment caused small but not significant decreases in turnover time.

The observed effects are best explained by the high concentrations of phosphorus and toxic chemicals that are present in the sediments but not extracted during the elutriation process. The high concentration of bacteria in the sediment and the physicochemical properties of sediments

may play an important role. These bioassays can be used to rapidly assess the potential toxic effects of dredged sediments, before disposal in open water.

INTRODUCTION:

The harbours of Lake Ontario have been dredged for navigation since the late 19th century. These harbour sediments contain extremely high concentrations of metals and other contaminants (Nriagu et al. 1983). Since open water disposal is the cheapest method (Iskandar et al., 1984), it has been the preferred way to dispose of contaminated sediments. Recent calculations show that the disposal of this dredged material contributes approximately 400000 metric tons per year of fine sediment to the sediment budget of Lake Ontario (Kemp and Harper, 1976).

Of major concern in the dumping of contaminated sediments is the potential for release of metals and other toxins and their effects on the lake biota at the dump site. The metals released and their concentrations depend on the chemical speciation and the physical conditions experienced during release (Mudroch and Davies, 1985). Metals tend to be associated with clay (<4 μ m) and silt (<63 μ m) sized particles (Mudroch, 1983) and these, especially the clay sized fraction, stay suspended the longest after dredging or dumping (Iskandar, et al., 1984).

Many metals are released during dredging or dumping operations (see for example Tramontano and Bohlen, 1984; Iskandar et al., 1984). A second effect of the dumping of sediments in open water is the alteration of the nutrient chemistry of the receiving water, especially with respect to phosphorus. Under aerobic conditions, such as those in the epilimnion of receiving waters, sediments tend to act as sinks for phosphate (Mortimer, 1971). However, Twinch and Peters (1984) showed that oxidized sediments can act as a source of phosphate if the phosphate concentration in the water is very low, as might occur as a result of biotic utilization.

The USEPA and Corps of Engineers developed the technique of sediment elutriation to simulate the release of sediment associated contaminants from dumped dredgeates (see Mudroch and Davies, 1985). Few studies to date have looked directly at the effects of sediment contaminants or sediment disposal on primary producers (see Flint and Lorefice, 1978; Munawar et al., 1983; Mayfield and Munawar, 1983). Only one study to date (Young et al., 1985) has looked at the release of algal available phosphate from suspended lake sediments.

Since the technique of sediment elutriation involves extracting contaminants from sediments with water and then separation of the sediment and water, the true effects of exposure of algae to sediments may not be seen as all of the contaminants may not be extracted. In addition, intimate

contact between the sediment particles and algal cells is prevented. In view of these reservations, we developed two bioassays, presented here, that directly assess the effects of sediment-associated contaminants on primary production and phosphorus kinetics. Both bioassays are based on the principle of directly exposing the algal cells to sediment particles and measuring the uptake of radio-isotope tracers in the presence of sediment.

The few studies of toxicity of metals and other sediment contaminants suffer from a serious drawback arising from the use of only one light intensity for experiments on photosynthesis and growth (see Munawar et al., 1983; Wong et al., 1982; Wong et al., 1985). This is inadequate for two reasons. Firstly, the effects of metals and other toxins, on photosynthesis and growth, may differ depending on the light conditions experienced by the phytoplankton.. Secondly, the photosynthetic rate at a single light intensity does not yield an accurate estimate of growth rate. The calculation of the light saturated photosynthetic rate (P_{max}), and Assimilation number is calculated as the rate of carbon fixation at P_{max} per unit chlorophyll a (Platt and Jassby, 1976) and is widely used to indirectly estimate phytoplankton growth rates (Cote and Platt, 1983).

METHODS:

Experimental Design and Sample Collection:

The effects of additions of elutriates and whole sediments on phytoplankton were investigated using natural assemblages from Lake Ontario. Time courses of photosynthesis and phosphate uptake were performed and the response of the photosynthesis vs. irradiance (P-I) relationship to these additions was examined. In all experiments, a correction was applied for the effect of dilution of the algae by the elutriate or sediment addition was corrected for by diluting the control bottles to the same degree with 0.2 μ m (Nuclepore) filtered lakewater (FLW). All additions of FLW or elutriates were done at a 10% (v/v) dosage. Sediment addition was done at a 2% (v/v) dosage as this is the amount of sediment in a 10% elutriate dosage. All experiments were run at the ambient lake temperature.

Sediment samples were collected from Toronto Harbour (Stn 1354) at Queen's Quay, using a Ponar grab sampler. These samples were placed in polyethylene containers for transport to the laboratory. Water samples were taken from immediately below the surface at an offshore station approximately 2 Km south-west of Toronto Island. These samples were placed in a 25L polyethylene carboy, darkened with black plastic bags, kept cool with ice and transported immediately to the laboratory.

Photosynthesis:

The effects of elutriate and sediment additions on the relationship between photosynthetic rate and irradiance (P-I) were examined. The rate of photosynthesis was measured using the ^{14}C method (Vollenweider, 1969). Filtered lake water, elutriate or sediment were added to 250mL of lakewater in 400mL polycarbonate bottles. These were spiked with 200 μl of dilute (20 $\mu\text{Ci/mL}$) ^{14}C - NaHCO_3 (Amersham 2mCi/mL). These bottles were arranged in series in a constant temperature box illuminated from one end with a 500W quartz halogen lamp. Irradiances ranged from less than 3.0×10^{14} to approximately 8×10^{16} quanta $\text{cm}^{-2}\text{s}^{-1}$. Bottles were incubated for 3-4 hours. All bottles were agitated at approximately 40 minute intervals. Irradiance was measured using a Model QSL-100 quantum meter (Biospherical Instruments Inc.). In bottles with sediment, the irradiance was measured at frequent intervals during the agitation cycle. Irradiance was then plotted against time and the curve was integrated using a Model 620000 planimeter (Keuffel and Esser Co.) to yield the average irradiance in each bottle.

At the end of the incubation, triplicate end-point filtrations of 50 mL were done on glass fibre (GF/C) filters (Whatman Ltd.). Filters were then frozen in glassine envelopes for later analysis. All treatments without sediment were also filtered, in triplicate, on 0.45 μm cellulose nitrate membrane (Sartorius Co.) filters. The filters were rinsed with lakewater filtered through GF/C filters, and dissolved in 15mL of PCS scintillation fluor (Amersham) in plastic vials. The radioactivity of the filters was later measured in a Beckman Model LS-6800 scintillation counter. The total amount of radioactivity added was measured in 1.0mL aliquots with 0.2mL of phenethylamine (Kodak Ltd.) added, and PCS as above.

In addition, two series were run to determine the effect of irradiance fluctuation caused by the settling of the sediment in the bottles. These series had 50mL screwcap test tubes glued in the centre of the bottles (Fig. 1). Lakewater (diluted with 10% FLW) was placed inside the tube and spiked with 50 μL of ^{14}C - HCO_3^- . In one series lake water was placed in the bottle outside tube and a 2% sediment-water mixture was placed outside the tube in the other series. In this way intimate contact between the phytoplankton and the sediment was prevented but the sediment still caused fluctuation of the irradiance levels. These series were filtered in duplicate (15mL aliquots) onto GF/C filters and frozen as above.

All glass fibre filters were later thawed and the photosynthate was extracted from the cells in 10 mL of dimethyl sulfoxide (DMSO) using the method of Shoaf and Lium (1976) modified by Burnison (1980). DMSO extracts were filtered onto GF/C filters and the filtrate was caught in 15mL plastic scintillation vials. To these vials 5mL of PCS fluor was added and radioactivity was measured as above.

Quench correction curves were calculated with DMSO,

chlorophyll and the coloured compounds extracted from the sediments by DMSO.

Phosphate Uptake:

The second bioassay measures the effect of sediment disposal on phosphorus kinetics in phytoplankton. The effects of elutriate and sediment addition on phosphorus uptake was examined in time-course experiments using carrier-free $^{32}\text{PO}_4\text{-P}$ (New England Nuclear Ltd) as a tracer (Lean and Nalewajko, 1976). Lakewater (200 mL) was incubated in the dark in 250 mL Pyrex reagent bottles. Over 1.5 hours, six aliquots were filtered onto both 0.2 μm and 1.0 μm pore size polycarbonate membrane (Nuclepore Corp.) filters. The 0.2 μm pore size filter entraps the entire biotic community while the 1.0 μm pore size filter approximates only the phytoplankton fraction. Filters were dissolved in 10 mL of PCS fluor in plastic vials and the radioactivity was measured as above.

Elutriates:

Sediment elutriates were prepared with the method of Mudroch and Davies (1985) from freshly obtained sediments. All filters used were pre-rinsed with 2x15 mL of deionized distilled water. Elutriates were made fresh on the day of experimentation. In the laboratory whole sediment was stored in the dark at 5°C, sealed in plastic bags.

All glassware was soaked for 24 hours in dilute (2%) H_2SO_4 and then rinsed six times with distilled water before use.

Data Analysis:

The photosynthetic data were compared with a Student's t-Test using the points that made up the light saturated portion of the P-I curve.

The phosphate data were compared by analysis of covariance (ANCOVA program Sokal and Rohlf, 1981) and then a Newmann-Kueller's test (Zar, 1974) to determine which treatments were significantly different. All statistics were computed with programs run on an Apple II+ and a DEC PDP-11 computer.

RESULTS:

Photosynthesis:

The results of the photosynthesis - irradiance curve for elutriate addition are shown in Figure 2. The addition of elutriate at a 10% (v/v) dosage had no effect on the initial, light limited part of the curve. However a 24% reduction in the light saturated photosynthetic rate (P_{max}) was seen.

This reduction was significant at $P < 0.05$.

Figure 3 shows the results of the DMSO extraction of ^{14}C -labelled photosynthate. The control series shows that 60% of all fixed ^{14}C was extracted by the DMSO. The incorporation of ^{14}C into photosynthate, at saturating irradiance levels, was depressed by 29% upon the addition of elutriate and this was significant ($P < 0.05$). However the addition of whole sediment caused much greater depression of P_{max} (81%). There was no effect on ^{14}C incorporation at light limiting irradiances.

It was important to ascertain whether the depression observed with the addition of whole sediment was due to the fluctuating light caused by the settling of the sediment or to toxic effects of the sediment itself. Figure 3 shows the results of the series run with the phytoplankton physically separated from the sediment. The series with just lakewater outside the test-tubes showed a significant ($P < 0.05$) 18% depression of P_{max} . The series with sediment outside the tube showed a 29% depression that was also significantly different from control, but not significantly different from the series with lakewater.

Phosphorus Kinetics:

The results of the ^{32}P uptake by the total assemblage ($< 0.2\mu\text{m}$) and the algal fraction ($< 1.0\mu\text{m}$) are shown, in Figures 3 and 4 respectively, as the % ^{32}P remaining in the filtrate. When plotted on a natural logarithmic scale the slope of the initial linear portion of the curve approximates the uptake rate constant (k). The reciprocal of this constant is the turnover time of the external phosphate pool. Turnover time is the time required for the algae to take up an amount of phosphate equal to that present. As such, it provides a good indication of the phosphorus status of the population as turnover time has been found to vary inversely with phosphorus demand (Lean and Nalewajko, 1979). The addition of elutriate caused large increases in turnover time in both the total and algal fractions. In both cases these increases were significantly different from control ($P < 0.05$). The addition of whole sediment caused very different results. There was an initial very rapid uptake of ^{32}P on the filters and then a return to levels similar to control where a near linear uptake was observed. This initial drop was omitted from the rate calculations. The rate of phosphate uptake upon the addition of whole sediment did not differ significantly from control in either the $> 0.2\mu\text{m}$ or $> 1.0\mu\text{m}$ fractions ($P < 0.05$). The values for turnover times of all treatments are shown in Table 1.

DISCUSSION:

It has been shown that the addition of elutriates or whole sediment causes decreases in the maximal photosynthetic rate

of epilimnetic phytoplankton. This depression was seen in both the total radiocarbon fixation and the amount of ^{14}C incorporated into DMSO extractable photosynthate. The depression was much greater in the treatments with whole sediment than those with elutriate. This great depression of photosynthesis could be expected as a result of the high levels of toxins present in these sediments. The sediments of Stn 1354 are known to be highly contaminated with both metals and organic toxins (MOE, 1985).

Filbin and Hough (1984) showed that DMSO will quantitatively extract labelled photosynthate from plant tissues with a high degree of accuracy. Extraction of this photosynthate allows measurement of the amount of ^{14}C fixed in the presence of whole sediment. The quenching caused by sediment makes direct scintillation counting of filters with sediment impossible while the quenching caused by DMSO is minimal. Thus the effects of exposure to sediments can be measured directly without the use of elutriates.

The lack of significant difference between the series with and without sediment around the test-tubes shows that the observed depression of P_{max} is due to the toxic effects of direct exposure of the algae to the sediment and not to the fluctuation in irradiance as the sediment settles.

Phosphorus Kinetics:

The results showed that the addition of elutriate caused significant increases in the turnover time of the external phosphate pool. This would be expected from the large concentrations of phosphate present in sediments and extracted during the elutriation process. An addition of phosphate will increase the phosphate pool and increase the turnover time. Oxidized sediments have been shown to release phosphate and this release seems dependent on the phosphate concentration in the receiving water (Twinch and Peters, 1984). Young et al. (1985) showed that large amounts of algal available phosphate are released from suspended lake sediments.

The rapid initial drop in amounts of ^{32}P remaining in the filtrate in treatments containing whole sediment are likely due to a rapid chemical diffusion of ^{32}P onto the sediment particles. Bacteria attached to the sediment particles may also play an important role in this movement of phosphate. The ^{32}P partitioning between sediment and water quickly reached equilibrium and a linear uptake of ^{32}P by the phytoplankton was seen. While whole sediment may release phosphate it also appears to act as a sink. Overall there was no significant effect on the algal uptake of phosphate. The difference between slowing of phosphate uptake by an increase in the PO_4 pool and by toxic effects of the sediment would seem to be hard to discern. However, if the reduction in phosphate uptake seen on elutriate addition was due to toxic effects, the same or more toxic effect would be expected upon the addition of whole sediment. This was not seen so it can be concluded that the primary effect of

exposure to sediments revolves around changes in the external phosphate pool and not poisoning of phosphate uptake mechanisms.

We have presented here two bioassays that permit rapid and direct assessment of the effects of sediment disposal on primary production and phosphorus kinetics. The uptake of ¹⁴C, in the presence of whole sediment can be measured by extraction of labelled photosynthate with DMSO. If this is done at a range of irradiance level an accurate picture of the effects on P_{max}, and therefore growth, can be achieved. Phosphorus kinetics can be affected by sediment in ways that differ from elutriate addition. This can now be directly assessed using the bioassay presented here.

Acknowledgements:

We wish to thank Dr. R. Boonstra for assistance with the statistical analysis and the field personel of Water Resources Branch, MOE. This work was supported by an MOE Grant to C. Nalewajko.

REFERENCES:

- Burnison B.K. (1980) Modified dimethyl sulfoxide (DMSO) extraction for chlorophyll analysis of phytoplankton. *Can. J. Fish. Aqua. Sci.* 37:729-733.
- Cote B. & T. Platt (1983) Day to day variations in the spring-summer photosynthetic parameters of coastal marine phytoplankton. *Limnol. & Oceanogr.* 28:320-344.
- Filbin G.J. & R.A. Hough (1984) Extraction of ¹⁴C-labeled photosynthate from aquatic plants with dimethyl sulfoxide (DMSO). *Limnol. & Oceanogr.* 29:426-428.
- Flint R.W. & G.J. Loreffice (1978) Elutriate-primary productivity bioassays of dredge spoil disposal in Lake Erie. *Water Res. Res.* 14:1159-1163.
- Iskandar I.K., J.H. Cragin, L.V. Parker & T.F. Jenkins (1984) Impact of dredging on water quality at Kewaunee Harbour, Wisconsin. US Army Corps of Engineers, Cold Regions Research & Engineering Laboratory. Report 84-21.
- Kemp A.L. & N.S. Harper (1976) Sedimentation rates and a sediment budget for Lake Ontario. *J. Great Lakes Res.* 2:324-340.
- Lean D.R.S. & C. Nalewajko (1976) Phosphate exchange and organic phosphorus excretion by freshwater algae. *J. Fish. Res. Bd.* 33:1312-1323
- & --- (1979) Phosphorus turnover time and phosphorus demand in large and small lakes. *Arch. Hydrobiol. Beih.* 13:120-132.
- Mayfield C.I. & M. Munawar (1983) Preliminary study of the effects of contaminants from sediments on algal membranes. *J. Great Lakes Res.* 9:314-316.
- MOE (1985) Historical development and quality of the Toronto Waterfront sediments - Part 1. Ministry of the Environment. May, 1985.
- Mortimer C.H. (1971) Chemical exchanges between sediments and water in the Great Lakes - speculations on probable regulatory mechanisms. *Limnol. & Oceanogr.* 16:387-404.

- Mudroch A. (1983) Distribution of major elements and metals in sediment cores from the western basin of Lake Ontario. *J. Great Lakes Res.* 9:125-133.
- & S. Davies (1984) Chemical speciation of metals in sediment elutriates. *Environ. Internat.* (in press).
- Munawar M., A. Mudroch, I.F. Munawar & R.L. Thomas (1983) The impact of sediment associated contaminants from the Niagara River mouth on various size assemblages of phytoplankton. *J. Great Lakes Res.* 9:303-313.
- Nriagu J.O., H.K.T. Wong & W.J. Snodgrass (1983) Historical records of metal pollution in sediments of Toronto and Hamilton Harbours. *J. Great Lakes Res.* 9:365-373.
- Platt T. & A.D. Jassby (1976) The relationship between photosynthesis and light for natural assemblages of coastal marine phytoplankton. *J. Phycol.* 12:421-430.
- Shoaf W.T. & B.W. Lium (1976) Improved extraction of chlorophyll a and b from algae using dimethyl sulfoxide. *Limnol. & Oceanogr.* 21:926-928.
- Sokal R.R. & F.J. Rohlf (1981) *Biometry* 2nd Ed. W.H. Freeman & Co. San Francisco.
- Tramontano J.M. & W.F. Bohlen (1984) The nutrient and trace metal geochemistry of a dredge plume. *Estuarine, Coastal & Shelf Science* 18:385-401.
- Twinch A.J. & R.H. Peters (1984) Phosphate exchange between littoral sediments and overlying water in an oligotrophic north-temperate Lake. *Can. J. Fish. Aqua. Sci.* 41:1609-1617.
- Vollenweider R.A. (1969) A manual on methods for measuring primary productivity in aquatic environments. IBP Handbook No. 12 Blackwell Scientific.
- Wong P.T.S., Y.K. Chau & D. Patel (1982) Physiological and biochemical responses of several freshwater algae to a mixture of metals. *Chemosphere* 11:367-376.

--- , --- & --- (1985) The use of algal batch and continuous culture techniques in metal toxicity study. Adv. Environ. Sci. Tecchnol. (in press).

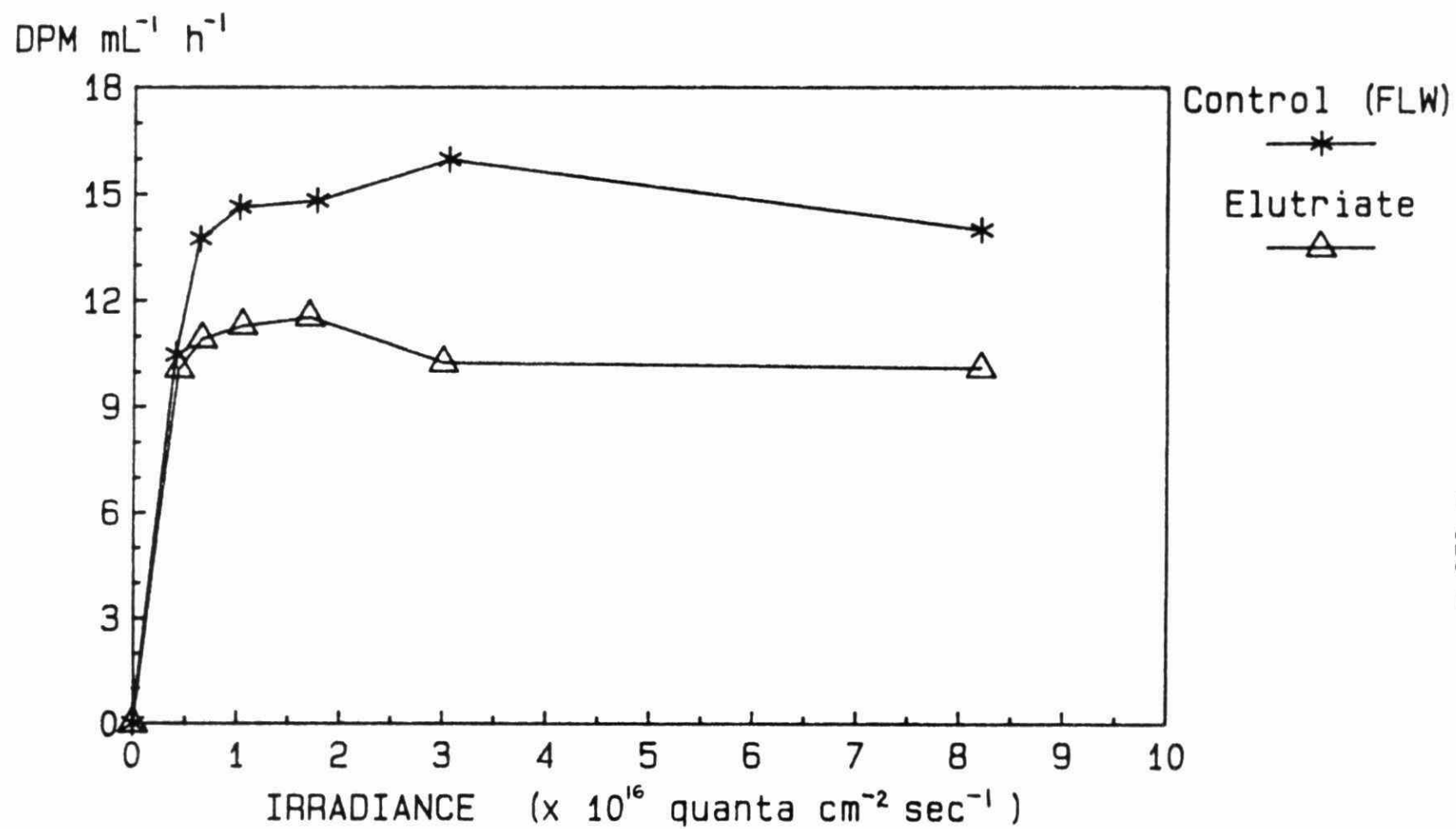
Young T.C., J.V. De Pinto, S.C. Martin & J.S. Bonner (1985) Algal-available particulate phosphorus in the Great Lakes Basin. J. Great Lakes Res. 11:434-446.

Zar J.H. (1981) Biostatistical Analysis. Prentice Hall.



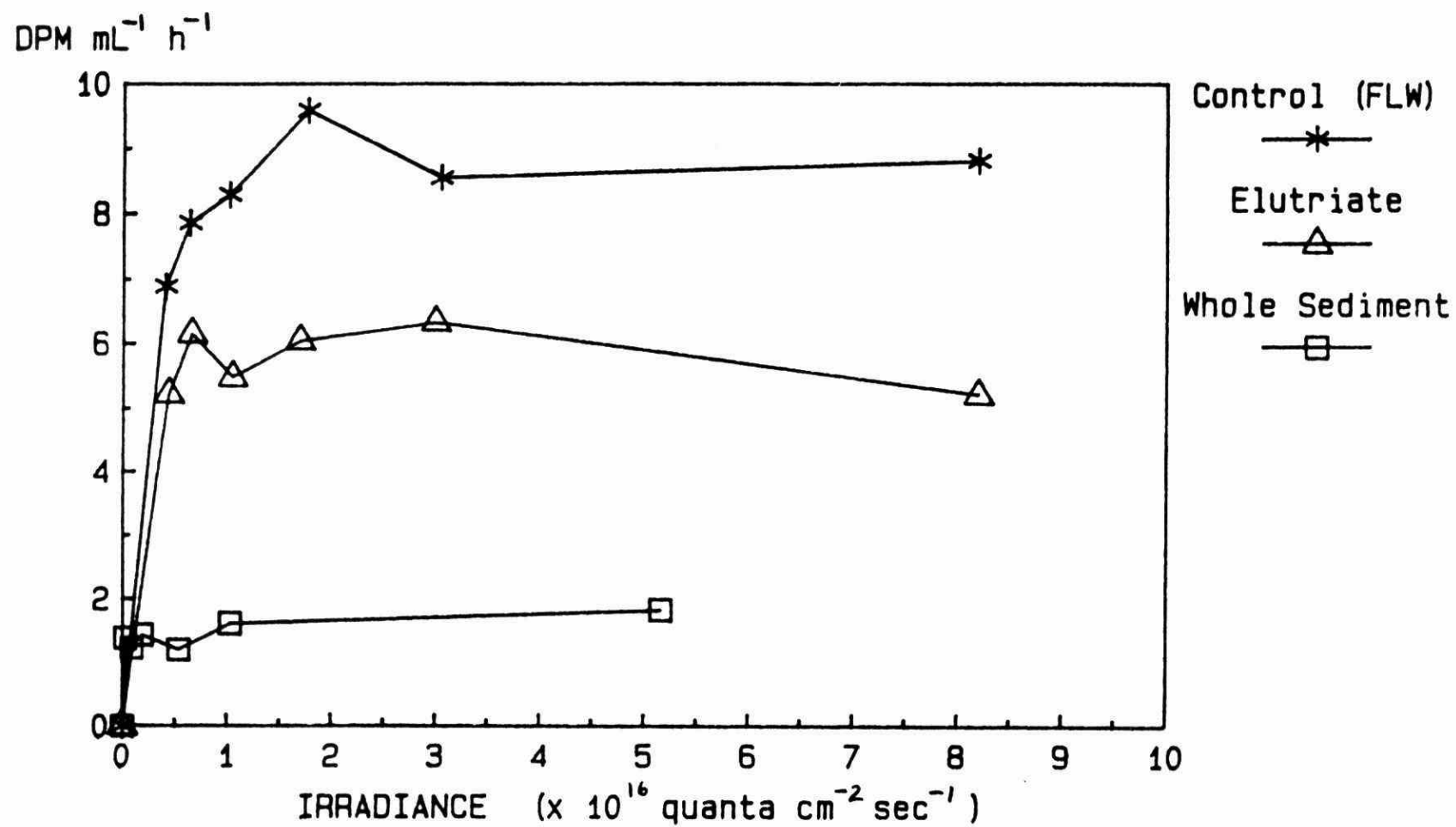
Figure 1: Constant temperature light gradient box used in P-I experiments. Experimental bottles with central test-tube (black) shown at front.

Figure 2: Photosynthesis -
irradiance curve of Lake Ontario
phytoplankton exposed to Stn 1354
sediment elutriate (10% v/v).



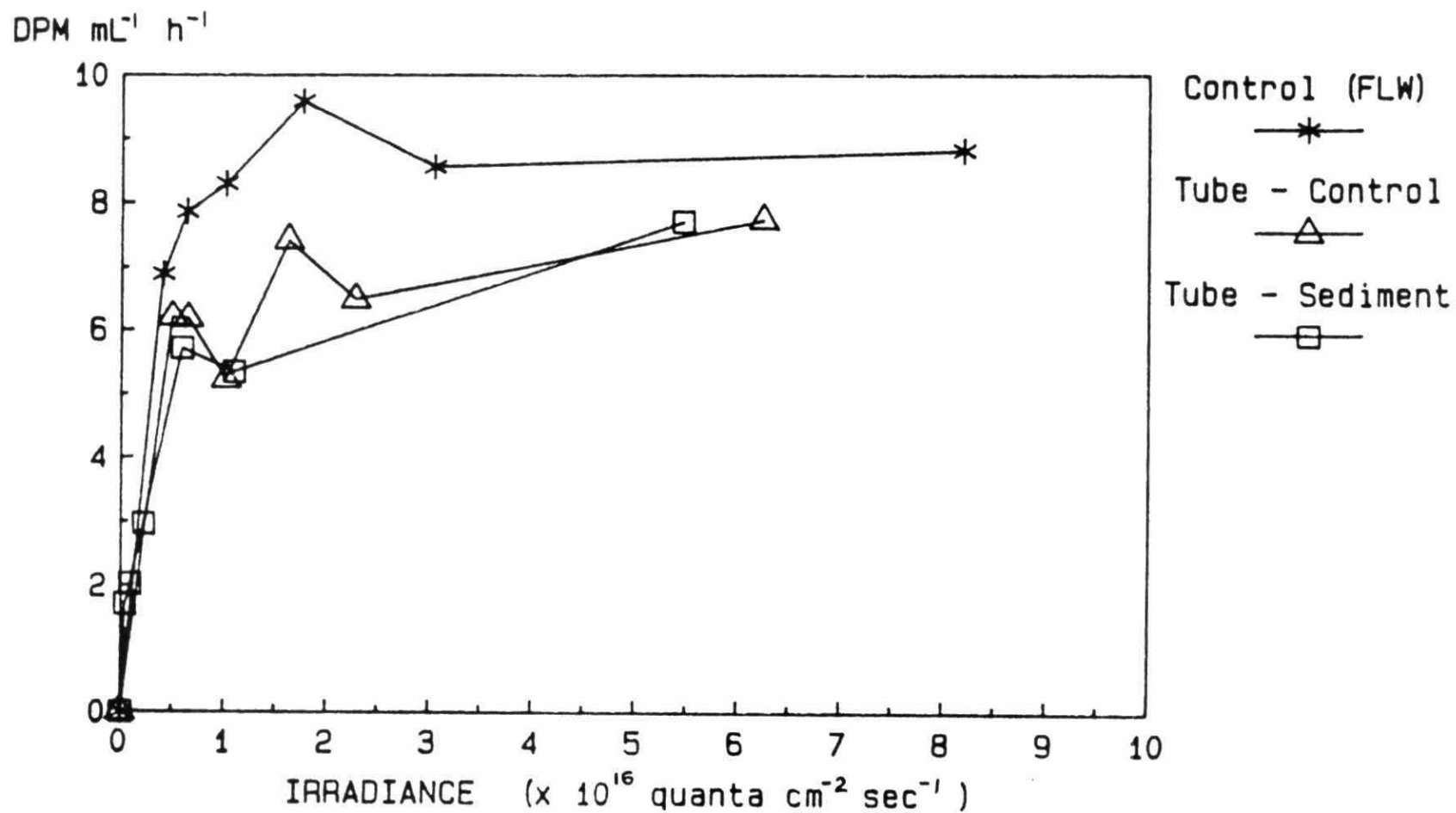
Filtered on 0.45µm Sartorius

Figure 3: Photosynthesis -
irradiance curve of ^{14}C -labelled
photosynthate extracted in DMSO from
Lake Ontario phytoplankton exposed to
Stn 1354 sediment elutriate (10% v/v)
and whole sediment (2% v/v).



Filtered on Wattman GF/C

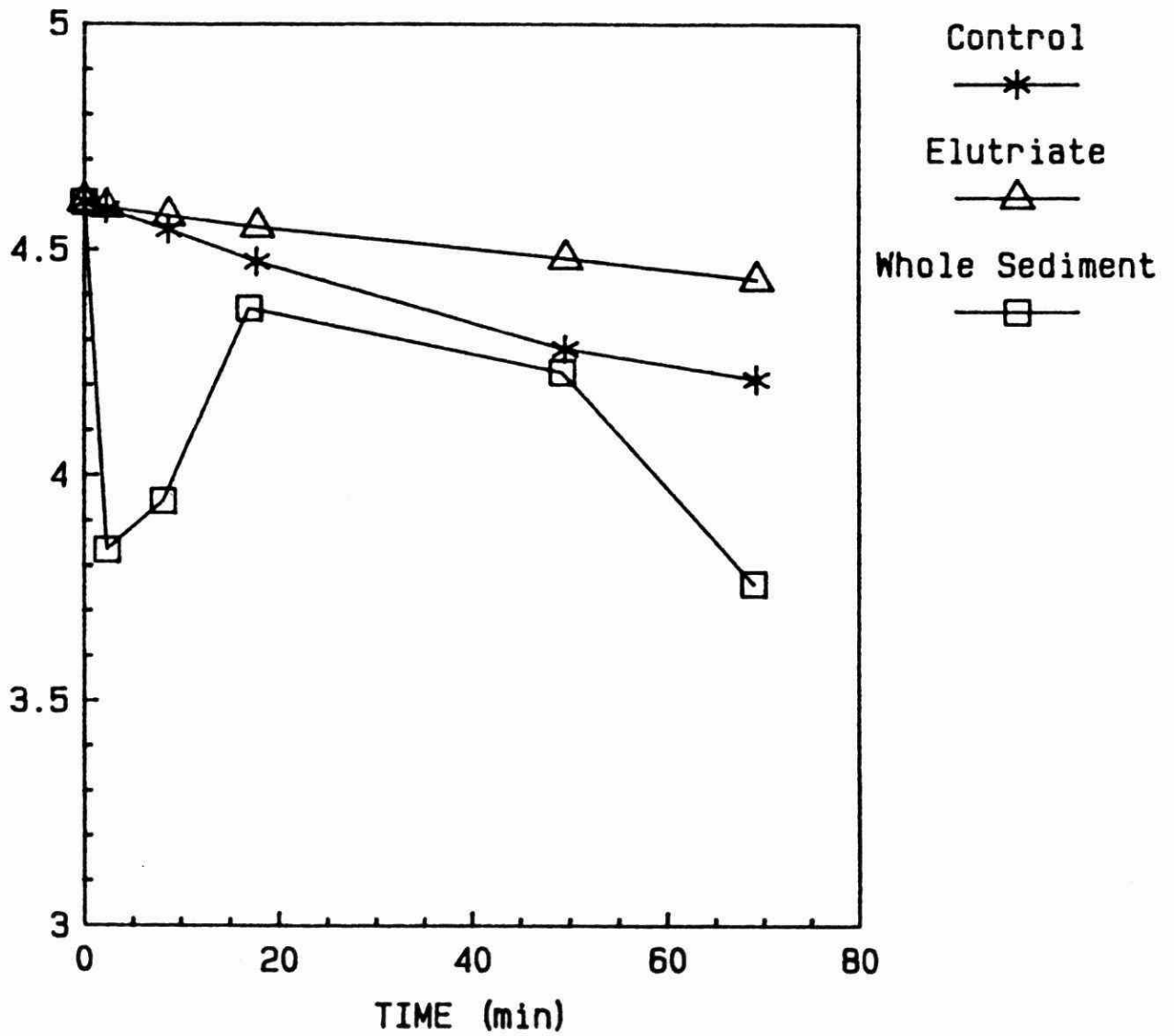
Figure 4: Photosynthesis -
irradiance curve of ^{14}C -labelled
photosynthate extracted in DMSO from
Lake Ontario phytoplankton incubated in
test-tubes shielded with lakewater or 2%
(v/v) sediment in lakewater.



Filtered on Wattman GF/C

Figure 5: Time course of ^{32}P
uptake by total assemblage of Lake
Ontario biota ($>0.2\mu\text{m}$) exposed to Stn
1354 sediment and sediment elutriate.

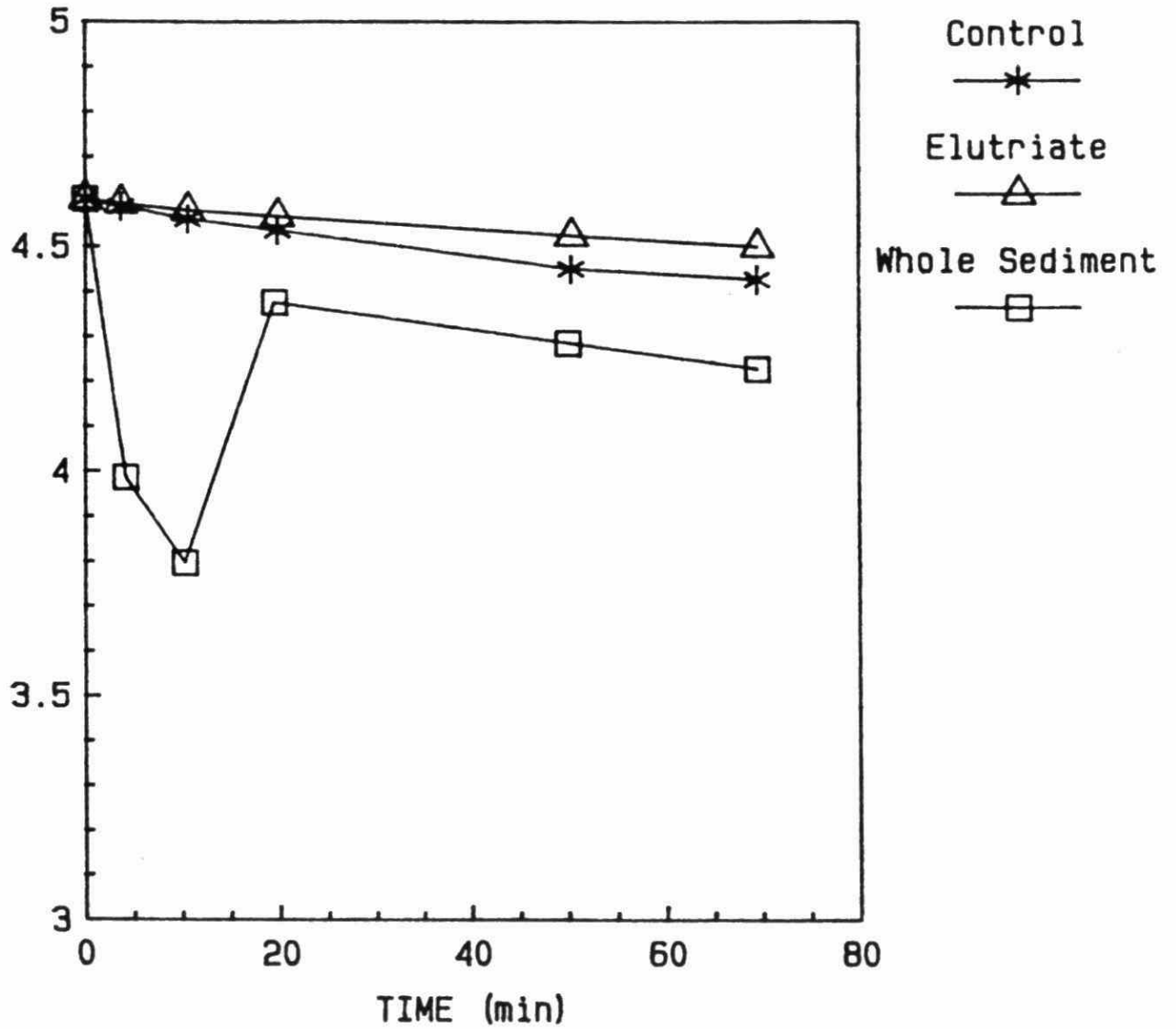
ln % ^{32}P Remaining



Filtered on 0.2 μm Nuclepore

Figure 6: Time course of ^{32}P
uptake by Lake Ontario phytoplankton
($>1.0\mu\text{m}$) exposed to Stn 1354 sediment
and sediment elutriate.

In % ^{32}P Remaining



Filtered on 1.0 μm Nuclepore

Table 1: Turnover times of ^{32}P uptake by Lake Ontario phytoplankton assemblages (Total and $>1.0\mu\text{m}$).

Treatment	Turnover time (min)	
	$>0.2\mu\text{m}$	$>1.0\mu\text{m}$
Control	152	330
Elutriate	414 *	634 *
Whole Sediment	138	336

'*' denotes significant difference from control at $p < 0.05$.

PROBABILITY AND STOCHASTIC MODELING OF WATER QUALITY PARAMETERS IN THE THAMES RIVER

V.A. Graham

Research Scientist
Department of Systems Design Engineering
University of Waterloo
Waterloo, Ontario, Canada.

T.E. Unny

Professor
Department of Civil Engineering
University of Waterloo
Waterloo, Ontario, Canada.

L. Logan

Chief, Hydrology Unit
Water Resources Branch
Ministry of the Environment
Toronto, Ontario, M4V 1P5

ABSTRACT

Models for the probability and stochastic behaviour of phosphorous and suspended sediment concentrations in the Thames river have been developed. The historic record of water quality parameters was observed to exhibit a strong non-Gaussian character, and to vary appreciably, depending on the month. Monthly probability distributions for these water quality parameters were described using a five parameter polynomial expression. This model will preserve the mean, variance, skewness, and kurtosis of monthly data. Owing to the non-Gaussian and varying nature of the monthly probability distributions, stochastic models were developed after transforming the data to a set representable by a single Gaussian distribution with constant statistics for all months. The novel transformation will allow almost all the statistical characteristics of the historic sequence to be preserved, since it incorporates the exact monthly probability distribution model of the historic sequence. Application of the ARIMA process to the transformed random variables reveal that an ARIMA[1,1,0] process is appropriate for transformed phosphorous data, and a white noise process for the transformed suspended sediment data.

INTRODUCTION

Quantifying the variations in water quality parameters is essential for developing water quality policy for reducing costly risk to the environment, due to stream-flow degradation. Presently, policy analysts and management are forced to rely on the use of historic records during the formation of policy guidelines, and in monitoring, regulating, and managing the concentration of toxic contaminants in Ontario streams. This approach involves the analyses of records of measured data in determining failure of established water quality criteria. Because water quality data are not deterministic, but random, the objective decision-making can become complicated.

The use of historic records in the work of monitoring and managing water quality is restrictive, in that only a small amount of useful information can be easily extracted. Management is generally limited to simple statistical indicators such as mean and standard deviation of water quality parameters over a period of time. Thus it is not possible to arrive at valuable information on the probability of events or the possibility that a given condition (for example, failure of water quality policy) will persist into future months. The formation of policy criteria for monitoring and managing water quality, however, does not necessarily demand that historic data be used. In fact, mathematical models which incorporate the salient probability feature of the historic record may be used to generate synthetic water quality data. By careful analysis of historical records it is possible to extract useful information on the character of the underlying probability distributions and the probability that a given condition may affect future events (ie. serial relationship between events), and imbed them into mathematical models.

These mathematical models for stream water quality, will allow for a flexible approach to evaluating policy failure; and make the assessing of risk to the environment accurate. They may also be used to provide an abundance of synthetic water quality data to be used in the evaluation of various management scenarios for improving water quality. And would enable projections of the water quality characteristics to be established, when the water

system is subjected to a known intervention. Because of the lack of reliable data (without missing values) such an evaluation is currently not possible.

These mathematical models form the subject of this paper. The development of models to characterize water quality uncertainties require rigorous analysis of the statistical and stochastic behaviour of water contaminant parameters. Statistical studies are needed to establish trends, moments, and probability distributions. Stochastic studies will allow the further information on the autocorrelation of successive events to be incorporated. This results of this research will provide a tool that will allow for greater objectivity in the decision making process, and a new approach, based on probabilities, to respond to failure of established water quality policy.

STATISTICAL BEHAVIOUR OF WATER QUALITY PARAMETERS

Models for water quality parameters will be constructed after detailed analysis of actual measured data. In the following the data set to be employed will be briefly described. Water quality data are collected by the Ontario Ministry of the Environment for a number of Canadian locations. These measurements generally include the average monthly concentration of water contaminants. Statistical and stochastic analysis of phosphorous concentration (P_c), and suspended sediments concentration (S_c) will be performed. Data, measured over a considerable time period (up to twenty years) is available. Unfortunately, the available data has a significant number of missing values. This loss of information may not hinder the model development work, but renders the use of pre-programmed computer codes (such as IMSL codes) useless; and requires greater care in extracting the relevant information for probability and stochastic modeling from contiguous data zones. Models will be constructed using data from the Thames rivers. Monthly record, collected over a period of twenty years will be used.

Statistical Analysis of P_c , and S_c

Any stochastic model for the water quality parameters must incorporate the salient statistical features of the historic data itself. Therefore, before model building is attempted, this data will be analyzed to determine its statistical properties. The statistical behaviour of water quality parameter values will be investigated by first studying the character of the principal moments: the mean, variance, skewness, and the excess kurtosis. These statistics are used to provide key information on the character of the underlying probability distribution and to assess closeness of the underlying distributions to Normally distributed random variables (information that is important in constructing stochastic models). Normally distributed random variables are specified by only two statistics, the mean and variance. Higher order moments, such as the skewness and kurtosis, are unique for Normally distributed random variables. In simple language, the skewness (g_1) provides a measure of the degree of symmetry (or lack of symmetry) about the mean. It measures the third central moment and, for a normally distributed random variable is equal to zero. The kurtosis measures the relative 'peakedness' of a distribution. It provides a measure of the fourth central moment and, for normally distributed random variables, is equal to 3. The excess kurtosis g_2 represents values of the fourth central moment greater or less than 3, and as such is zero for Normally distributed random variables. Estimates of the skewness and kurtosis for an arbitrary random variable x is obtained as follows:

$$g_1 = \frac{\frac{1}{N} \sum_{i=1}^N [x_i - \bar{x}]^3}{\left(\frac{1}{N} \sum_{i=1}^N [x_i - \bar{x}]^2 \right)^{3/2}} \quad g_2 = \frac{\frac{1}{N} \sum_{i=1}^N [x_i - \bar{x}]^4}{\left(\frac{1}{N} \sum_{i=1}^N [x_i - \bar{x}]^2 \right)^2} - 3 \quad 1$$

where N is the total number of x values.

These statistics will be computed using monthly data P_c and S_c occurring over twenty years, for the Thames river. Special care was necessary in computing these statistics, owing to the presence of missing values in the data. Summary statistics of the random variables are

presented in the Table 1 and 2.

TABLE 1				
STATISTICS FOR MONTHLY PHOSPHOROUS CONCENTRATION P_c THAMES RIVER				
MONTH	MEAN \bar{P}_c	STD. DEVIATION σ_P	SKEWNESS $g_{1,P}$	KURTOSIS $g_{2,P}$
Jan	0.357	0.346	2.748	7.458
Feb	0.332	0.253	1.711	1.953
Mar	0.344	0.325	3.241	10.199
Apr	0.249	0.123	1.518	2.777
May	0.316	0.197	0.732	-0.606
Jun	0.599	0.535	0.935	-0.459
Jul	0.452	0.487	1.701	2.202
Aug	0.596	0.594	1.743	2.381
Sep	0.504	0.387	0.685	-0.864
Oct	0.431	0.516	1.989	2.715
Nov	0.352	0.281	1.403	0.867
Dec	0.240	0.179	1.631	2.083

TABLE 2				
STATISTICS FOR MONTHLY SEDIMENTS CONCENTRATIONS S_c THAMES RIVER				
MONTH	MEAN \bar{S}_c	STD. DEVIATION σ_S	SKEWNESS $g_{1,S}$	KURTOSIS $g_{2,S}$
Jan	8.657	5.559	1.357	1.038
Feb	9.506	4.658	0.124	-1.240
Mar	18.865	16.100	1.765	2.529
Apr	20.031	18.236	3.025	8.523
May	22.193	32.835	3.201	8.556
Jun	17.969	7.614	0.292	-1.065
Jul	19.427	9.308	1.491	1.814
Aug	19.464	8.985	0.182	-1.467
Sep	23.773	12.032	0.971	1.234
Oct	17.147	6.174	-0.019	-1.255
Nov	17.350	8.338	1.778	2.039
Dec	12.484	7.007	0.289	-1.121

The statistics estimated indicate appreciable variation in the monthly mean, \bar{P}_c , and \bar{S}_c throughout the year. The monthly standard deviation, skewness, and kurtosis are also observed to change significantly from month-to-month. This variation in moment estimates tells us that the probability distribution of each of these random variables are not the same for all months. If the random variables had a constant distribution for all

months, then moments estimates would be the same for all months. Since this is not the case it follows that the probability distributions are changing from month-to-month. Thus a procedure which uses annual means and variance etc. (which implies a fixed probability distribution) in policy decision making, could be very misleading, and could mask serious and persistent violations of policy guidelines for specific seasons in the year.

Accurate stochastic models for the random variables should reproduce much of these statistics, if the models are expected to represent the process. Thus the process itself changes monthly, and hence is nonstationary. This may be so partly because variable such as stream flow, which affects the concentration of water quality parameters, varies seasonally, depending on factors as snow melt or precipitation. Incorporating the probability features of the historic data in stochastic models will require some mathematical description. Developing suitable mathematical representations for the water contaminants is the subject of the following section.

Probability Model for Water Quality Parameters, P_c and S_c

Since the probability distributions of the random variables is found to vary monthly, it is not possible to arrive at a fixed distribution function for all months. In this study probability functions for monthly random variables will be sought. In the development of probability models it is possible to empirically determine frequency functions and fit equations to these curves. However, a more appropriate way is to determine the density function using the moments itself (Frazer, 1976). In this way density functions are guaranteed to reproduce the key moments of the historic data.

If $P[x]$ denote the true density of random variable x , (The variable x is used to represent any one of P_c , and S_c .) and $p(x)$ used to represent a mathematical approximation of the density function $P[x]$, then $p(x)$ must be chosen to preserve the moments of the unknown $P(x)$ that is important to the problem at hand. In our work probability models are needed to infer cumulative probability estimates of monthly events, and to preserve the principal moments in synthetic water quality data, generated

using a developed stochastic model. Thus a simple polynomial representation for the monthly density function may be used. The polynomial density function which exactly reproduces the estimated moments of historic data will be used to represent the data. The approximate polynomial density can be expressed as

$$p[x] = \sum_{i=0}^n c_i x^i \quad 2$$

Our quest is to identify $p(x)$ such that the i^{th} moment is conserved. The coefficients c_i must be so chosen that the sum of squares function $J(c_0, c_1, \dots, c_n)$ is minimized. The sum of squares function is defined as follows:

$$J(c_0, c_1, \dots, c_n) = \int_{x_l}^{x_u} [P(x) - p(x)]^2 dx \quad 3$$

The coefficients c_i are obtained by solving the system of equations resulting from

$$\frac{\partial J}{\partial c_i} = 0 \quad i=0,1,2,\dots \quad 4$$

It is desired that the first four moments need be conserved, hence the approximate polynomial density expression will have only five parameters, that is, $n=4$. Also by noting that

$$\int_{x_l}^{x_u} x^i P(x) dx = \mu_i \quad 5$$

where $\mu_0=1$, μ_1 is the mean, and \bar{x} provides an estimate of it; μ_2 is the second moment about the origin, and can be estimated from the variance σ^2 ; μ_3 and μ_4 are the third and fourth moments about the origin, respectively, and can be estimated from the skewness and kurtosis, respectively. The above set of equations, after substituting for $p(x)$ and integrating, simplify to the following set of system of equations

$$P C = M$$

6

where

$$P = \begin{bmatrix} p_1 & p_2 & p_3 & p_4 & p_5 \\ p_2 & p_3 & p_4 & p_5 & p_6 \\ p_3 & p_4 & p_5 & p_6 & p_7 \\ p_4 & p_5 & p_6 & p_7 & p_8 \\ p_5 & p_6 & p_7 & p_8 & p_9 \end{bmatrix} \quad C = \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} \quad M = \begin{bmatrix} 1 \\ \mu_1 \\ \mu_2 \\ \mu_3 \\ \mu_4 \end{bmatrix} \quad 7$$

and $p_i = \frac{x_u^i - x_l^i}{i}$; μ_2 , μ_3 , and μ_4 are the second, third, and fourth moments of x about the origin, respectively.

and the coefficients c_i are obtained after inversion:

$$C = P^{-1}M \quad 8$$

The moments about the origin can be estimated from the central moments estimated in Tables 1 and 2. Values of x_u and x_l necessary to evaluate integrations involving the polynomial density function were obtained by setting them to the corresponding extremes observed after 20 years.

TABLE 4		
TWENTY YEAR EXTREME VALUES OF TOXIC CONCENTRATION IN THAMES RIVER		
Variable	x_u (MG/L)	x_l (MG/L)
Phosphorous	2.353	0.059
Sediments	135.0	2.000

The polynomial model was observed to reproduce the first four moments exactly, and to produce a distribution function with total probability of unity. The model, however, has the difficulty that it does not guarantee a smooth density function, with limited turning points as would exist in practice.

STOCHASTIC MODEL CONSTRUCTION

Stochastic models of the water quality variables, will be addressed by studying the phosphorous and suspended sediment concentrations separately. The series of water quality parameters is a nonstationary series: the series are shown to be governed by different non-Gaussian probability distributions for different months. An accurate stochastic model requires maintaining the salient probability characteristics of historic record; these include maintaining the monthly varying mean, variance, skewness, and kurtosis. This is done most effectively if the monthly marginal distribution is incorporated in the modeling activity. Thus, the principal moments (mean, variance, skewness, kurtosis, and higher order moments) will automatically be preserved in synthetic sets of water quality parameters generated using these models. Owing to this complex nonstationary behaviour of monthly water quality parameters and further because the series are non Gaussian, direct application of the ARIMA process is not appropriate.

Various methods have been suggested in the literature for correcting nonstationary behaviour in stochastic series. The method of differencing is a popular approach. While differencing can correct some forms of nonstationarity, it requires that the original series be Gaussian. Another method for correcting nonstationary behaviour in stochastic series is the method of deseasonalizing the series (eg. Tao and Delleur, 1975, Hipel et al, 1977). This method will produce a series that is stationary in the mean, and having constant variance—that is, having zero mean and unit variance. If these were the only two properties desired to be reproduced in synthetic water quality data, then the deseasonalizing method would be appropriate. But because deseasonalization is a linear transformation, higher order moments of the transformed series will still be varying throughout the year. The use of a power (non-linear) transformation such as the transformation due to Box and Cox (1964) is also quite popular for rendering inherently non-Gaussian series approximately Gaussian; but since the distribution of monthly water quality events changes monthly, a single power transformation would be inappropriate.

Others (eg. Hipel and McLeod, 1979) have suggested applying Fourier analysis to estimate time varying trends in the data, and modeling the resultant series. This approach is useful primarily when there are known cyclic trends imbedded in the series. It is not applicable to the water quality parameters under investigation since the distribution of the detrended set also will be non-Gaussian and time varying.

The popular transformation procedures, namely, differencing, or deseasonalizing may not accurately correct for non-stationarity of monthly water quality parameter, and also render the series representable by a Gaussian distribution. To do this novel methods must be applied. The problem at hand requires transforming the series to a stationary set that is representable by a single Gaussian distribution. This problem can be solved if the random variable were to be transformed into a new random variable that is Gaussian, using the actual probability distributions for the random variable.

Probability Integral Transformation

Before the ARIMA process can be applied it is necessary to correct for the non-Gaussian and monthly varying probability distribution in water quality parameters series. These objectives can be attained if these random variable were to be transformed into a new Gaussian random variable with invariant statistics— with an equal mean and variance, for all months. The transformation functions must be chosen in such a way as to map monthly sets of water quality data from its parent distribution to this new Gaussian domain. But since the distribution for water quality parameters (say x) changes monthly, the transformation must also change monthly. If $x_{t,j}$ denotes a measure of water quality in month j and, $\zeta_{t,j}$ denote Gaussian variable corresponding to the same month, and f_j denote the monthly transformation function, then

$$f_j[x_{t,j}] = \zeta_{t,j} \quad 9$$

For simplicity the mean and variance of the Gaussian distribution for ζ will be chosen to be 0 and 1, respectively, for all months. Therefore, the annual set of $\{\zeta_{t,j}\}$ will be $N[0,1]$.

In this problem the densities of both variables are known, but the transformation functions are unknown. The functional relationship between $\varsigma_{t,j}$ and $x_{t,j}$ requires that the mapping, between the Gaussian distribution and the distribution for $x_{t,j}$, be done in such a way as to ensure that the marginal probability is unaltered. Let $g[\varsigma_{t,j}]$ denote the single marginal Gaussian density function of $\varsigma_{t,j}$, in all months and $P_j[x_{t,j}]$ the monthly density function of $x_{t,j}$. Now, if a new variable $u_{t,j}$ is defined such that it is assigned the cumulative probability of $\varsigma_{t,j}$, then

$$u_{t,j} = \int_{-\infty}^{\varsigma_{t,j}} g(t)dt = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\varsigma_{t,j}} e^{-\frac{t^2}{2}} dt = \frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{\varsigma_{t,j}}{\sqrt{2}}\right) \right] \quad 10$$

It can be shown (Blake, 1979) that values of $u_{t,j}$ will be uniformly distributed on the interval (0,1). Also if another variable $v_{t,j}$ is defined such that it is assigned the cumulative probability of $x_{t,j}$, then

$$v_{t,j} = \int_{x_t}^{x_{t,j}} P[x_{t,j}]dx_{t,j} = F(x_{t,j}) \quad 11$$

Again it can also be shown that values of $v_{t,j}$ will be uniformly distributed, on the (0,1) interval. (Random variables which are transformed by their distribution function always yield a transformed variable that is uniformly distributed.) Since the random variable $u_{t,j}$ and $v_{t,j}$ are represented by the same distribution, for all time t and for a specific month j , and the sought transformation requires that the cumulative probabilities be maintained, it follows that for the same value of t,j : $u_{t,j}=v_{t,j}$. Hence, integral transformations may be equated to give the desired transformation function f_j for mapping between $\varsigma_{t,j}$ and $x_{t,j}$.

$$\frac{1}{2} \left[1 + \operatorname{erf}\frac{\varsigma_{t,j}}{\sqrt{2}} \right] = \int_{x_t}^{x_{t,j}} P[x_{t,j}]dx_{t,j} = F(x_{t,j}) \quad 12$$

Hence,

$$\varsigma_{t,j} = f_j[x_{t,j}] = \sqrt{2}\operatorname{erf}^{-1}\left[2F(x_{t,j})-1\right] \quad 13$$

The transformation function is therefore defined by equation 13, and requires only monthly values of c_i to specify the probability density function (eq. 2) for the water quality variable, prior to performing the integration of equation 31. Computation of the inverse error function is discussed in Strecok (1968).

Therefore the transformation function can be computed by first computing the cumulative probability $F[x_{t,j}]$ and further substituting this value in equation 13. This transformation will yield a series with a $N[0,1]$ distribution. The series of $\zeta_{t,j}$ data will have constant marginal statistics for all parts of the series: the monthly mean, variance, skewness, kurtosis, etc. will all be the same—a prerequisite for applying the ARIMA process to the data. Since the transformation was chosen so that the statistics of the transformed variable are invariant with time, the subscript j on $\zeta_{t,j}$ may be dropped.

ARIMA Stochastic Process Modeling

Given that the transformed variable is Gaussian with zero mean, variance unity, the ARIMA stochastic difference equation is now relevant to constructing a model for this variable. The system of difference equations for the transformed variable is

$$\phi(B)(1 - B)^d \zeta_t = \theta(B)w_t \quad 14$$

where w_t is a Gaussian white noise process; B is a backward shift operator defined by $B^r \zeta_t = \zeta_{t-r}$; $\phi(B)$ and $\theta(B)$ are polynomials in B defined by

$$\theta(B) = 1 - \theta_1 B - \theta_2 B^2 - \dots - \theta_q B^q \quad 15$$

$$\phi(B) = 1 - \phi_1 B - \phi_2 B^2 - \dots - \phi_p B^p \quad 16$$

If the differenced variable (ie. $(1-B)^d \zeta_t$) is denoted z_t then the stochastic difference equation is appropriately recast as

$$z_t - \sum_{r=1}^p \phi_r z_{t-r} = w_t - \sum_{r=1}^q \theta_r w_{t-r} \quad 17$$

This research will assume that the stochastic process for ζ_t may be modeled as having a

time invariant autocorrelation structure. A condensed list of the important steps to be followed in applying the $ARIMA[p,d,q]$ process to modeling the historical ζ_t series is given by Unny (1977) and Hipel et al (1977). Model construction details are discussed in Box and Jenkins (1970) and Anderson (1976).

System Identification

Identifying the system equations involves studying the stochastic structure of the annual ζ_t series to determine the class of models which may be used to represent the data, and which models are worthy of further investigation. The main aim is to obtain an idea of the values of p , d , and q needed in the system equations. The principal tools are the autocorrelation and partial autocorrelation function.

The autocorrelation function ρ_τ in the ζ_t data was studied by forming sets of $\{\zeta_t, \zeta_{t+\tau}\}$ for $\tau=1$ to 20, and computing the estimated correlation coefficients $\hat{\rho}_\tau$. In this way the linear relationship between values of the transformed variable occurring in month t and values occurring τ previous months to it was studied. These values were computed using twenty years of monthly ζ_t data (or differenced ζ data). Estimates were obtained using a computer program which systematically extracted the autocorrelation information from zones in the data set where there was no missing data. To identify a model, it is necessary to use estimates $\hat{\rho}_\tau$ to check on whether the autocorrelations are rapidly decaying, or is there any trends. The presence of non-decaying autocorrelation estimates usually indicate the presence of trends, which often suggests the need to difference the data further. If the autocorrelation estimates are decaying, it is also necessary to determine when these estimates are effectively zero beyond a certain lag, τ . For this purpose Bartlett's (1946) approximate expression for the variance of the estimated autocorrelation coefficients of a stationary Normal process can be used to test the statistical significance of autocorrelation estimates.

$$\text{var}[\hat{\rho}_\tau] = \frac{1}{N} \left[1 + 2 \sum_{v=1}^q \hat{\rho}_v^2 \right] \quad \tau > q \quad 18$$

If the hypothesis is tested that the process is white noise, that is, ρ_τ is zero for $q > 0$ then the standard error associated with all autocorrelation estimates $\hat{\rho}_\tau$ beyond τ equal to zero, will be approximately $(1/N)^{1/2}$; and with N being of the order of 190 (when missing values and loss of information due to differencing are accounted for) the standard error will be approximately 0.073. Figures 1-4 show plots of the autocorrelation at different levels of differencing of Phosphorous and Suspended Sediments in the Thames river. From these plots it is seen that the autocorrelation function for transformed phosphorous data fails to die out, but is significant up to 20 lags. This suggests that the data ought to be differenced. Figure 2 shows that the autocorrelation estimates died out quickly after the first differencing. Additional differencing of this data, as shown in Fig. 3, did not provide for any reduction in the autocorrelation estimates. It was therefore concluded that differencing only once was necessary. On the other hand, when Suspended Sediment data was studied, the autocorrelation estimates of the transformed data all appeared to be insignificant. This suggests that the underlying process is random, and future events does not depend on the time history of the process.

Partial Autocorrelation Function

Before more can be said about the class of models to be entertained it is required to study the partial autocorrelation function. This is done by computing the last parameter in different autoregressive schemes. The class of models to be entertained is determined by studying this quantity (the pacf) in conjunction with the autocorrelation function. The stochastic process may be identified when the last term in an autoregressive scheme is such that estimates for subsequent terms are statistically zero. This activity is an iterative one; it involves assuming different autoregressive schemes to fit to the data, and using the autocorrelation estimates, compute the value of the last parameter in the model. Partial autocorrelation estimates, for values for models of order up to 20, are

often required to identify the appropriate model. Obtaining these by solving the Yule-Walker equations can be cumbersome, and costly in computer time; therefore they were computed using a recursive formulae due to Durbin (1960). Durbin's method uses past estimates of the partial autocorrelation function to estimate future values. Thus parameter estimates for an AR[p+1] process are obtained using known estimates of the parameter of an AR[p] process, fitted to the same data. Durbin's formulae are presented as follows:

$$\hat{\phi}_{(p+1)(p+1)} = \frac{r_{p+1} - \sum_{j=1}^p \hat{\phi}_{pj} r_{p+1-j}}{1 - \sum_{j=1}^p \hat{\phi}_{pj} r_j} \quad 19$$

$$\hat{\phi}_{(p+1)j} = \hat{\phi}_{pj} - \hat{\phi}_{(p+1)(p+1)} \hat{\phi}_{p(p-j+1)} \quad j=1,2,\dots,p \quad 20$$

Other recursive methods for estimating the partial autocorrelation function have been developed (Pagano, 1973).

Estimates, $\hat{\phi}_{pp}$, of the partial autocorrelation can be obtained by using $p=1,2,3,\dots$ in equations 19 and 20. These values are then studied to determine when they become statistically indifferent from zero.

Quenouille (1949) states that at large values of τ , the estimated partial autocorrelation is asymptotically normally distributed:

$$\hat{\phi}_{\tau\tau} \sim N\left\{0, \frac{1}{N}\right\}, \quad \tau > p \quad 21$$

Thus if an autoregressive process is of order p , the estimated partial autocorrelation for an order $p+1$ and higher will be independently distributed with standard error $S.E.[\hat{\phi}_{\tau\tau}]$ of $1/\sqrt{N}$. With N being approximately 190, then Quenouille's formula indicate that twice the standard error of $\phi_{\tau\tau}$ is of the order of 0.15.

Figures 5 and 6 show plots of the partial autocorrelation function for Phosphorous and Suspended Sediments with 95% confidence limits, assuming an hypothesis that they are all zero. The plot for Phosphorous reveal that beyond lag 3 the partial autocorrelation estimates are approximately zero for phosphorous concentration. However, the partial autocorrelation estimates for Suspended Sediments are again insignificant for all lags, thus confirming that all parameters in an autoregressive scheme is statistical zero— hence the process is white noise. Theoretical processes which reveal a truncating partial autocorrelation function are purely autoregressive. Processes with moving average terms have slowly decaying partial autocorrelation function.

The estimated autocorrelation function and the estimated partial autocorrelation function for the differenced data suggest that the process for transformed monthly phosphorous data is autoregressive, and require approximately two (or at most three) parameters for its description. These estimates are, however, themselves correlated and as such should be used only to indicate the type, and neighborhood of the models that should be considered. In general it is necessary to entertain other models than the one indicated to ensure that the most appropriate model, and parsimous model is selected to represent the data. In addition to the ARMA[2,1,0] model, ARMA[3,1,0], and an ARMA[1,1,0] will also be entertained.

Parameter Estimation

Having identified the set of models to be entertained, it is necessary to estimate the parameters in these models, and select the model which fits the data best. There are numerous methods that may be used to estimate the model parameters. The method recommended by Box and Jenkins (1970), and which will be used, is the method of maximum likelihood. Since the variance of ζ_t is constant, and the model is linear, the variance of w_t will also be constant, hence, the conditional log-likelihood function can therefore be studied by studying the conditional sum of squares function. The parameter estimates will therefore be those that minimizes the sum of squares function, or the noise variance. The residuals are the set $\{\hat{w}_t\}$ which minimizes the sum of squares function.

They are obtained using

$$\hat{w}_t = \zeta_t - \hat{\zeta}_t \quad 22$$

where $\hat{\zeta}_t$ are generated values, obtained using the parameter estimates, and ζ_t is the actual data. Different sets $\{\hat{w}_t\}$ can be obtained for various values of (ϕ, θ) . The estimation process is made efficient by using a non-linear least squares procedures.

The computation of the sum of squares function is conditional on the starting values for w_t used. For very short series, the transients introduced by the choice of this value, in synthetic data will be significant. However, for fairly long series, the unconditional likelihood function is approximated by the likelihood function, if suitable starting values w_* and ζ_* are selected (Box and Jenkins, 1970). For most applications the starting values are set to their unconditional expectation: $E[w_*] = 0$. The parameter estimates will be obtained using zero for the value of w_1 .

A modified steepest descent algorithm (IMSL) was used to provide efficient estimates of the parameters that minimized the sum of squares (or noise variance). The estimation was performed using double precision arithmetic. Special care was again necessary, to ensure that the estimation was performed only from zones in the data without missing values. The following tables show summary results from applying ARIMA[1,1,0], ARIMA[2,1,0], and ARIMA[3,1,0] models to ζ .

TABLE 4 ARIMA [p,d,q] MODELS FITTED TO TRANSFORMED PHOSPHOROUS DATA				
ARIMA[p,d,q] MODEL	PARAM.	PARAM. EST.	PARAM. STD. ERR.	NOISE VAR., σ_w^2
$(1-B)(1-\phi_1 B)\zeta_t = w_t$	ϕ_1	-0.546	0.060	0.501
$(1-B)(1-\phi_1 B - \phi_2 B^2)\zeta_t = w_t$	ϕ_1 ϕ_2	-0.679 -0.284	0.054 0.071	0.460
$(1-B)(1-\phi_1 B - \phi_2 B^2 - \phi_3 B^3)\zeta_t = w_t$	ϕ_1 ϕ_2 ϕ_3	-0.725 -0.270 -0.500E-15	0.052 0.073 0.076	0.450

The standard errors of the parameter estimates listed in Table 6 was obtained using the following (Anderson, 1976).

$$ARMA[1,0] : \sigma_\phi^2 = \frac{1 - \phi^2}{N} \quad ARMA[2,0] : \sigma_{\phi_1}^2 = \sigma_{\phi_2}^2 = \frac{1 - \phi_2^2}{N} \quad 23$$

A study of the residual variances for the models listed in Table 6 reveal very slight (if any) decrease in unexplained variability for the ARIMA[3,1,0] or ARIMA[2,1,0] models over the ARIMA[2,1,0] model. Anderson (1976) applied the F statistic to give a crude comparison between these noise variances. To test if the ARIMA[3,1,0] model, produces a noise variance that is significantly different from the ARIMA[2,1,0], the computed F will be $(0.46/0.45)^2$, which is 1.045. Testing the hypothesis of equal variance at the 5% significant level, shows $F_{194,183}$, from standard tables, being greater than 1.002. Hence, the variance estimators are not significantly different. A comparison with the ARIMA[1,1,0] model and the ARIMA[2,1,0] model also reveals little or no difference in noise variance. Applying the F test to the ARIMA[1,1,0] and ARIMA[2,1,0] models yields a F statistic of 1.18; and when its significance was tested at the 5% level the difference could have occurred by chance. Hence the most parsimous model for transformed monthly phosphorous data is the ARIMA[1,1,0] model; it is also very significant, since its

parameter is approximately eight times its standard error.

Generating Synthetic Water Quality Data

The stochastic models for phosphorous and suspended sediments may be used to generate synthetic water quality data for these monthly events. To do this, it will first be necessary to generate an uncorrelated set of random Gaussian deviates for the w_t process. Many methods for doing this is reported in the literature, examples of which are Marsaglia and Bray (1964), Atkinson and Pierce (1976), and Lewis et al (1969). These white noise random variables are then substituted in the stochastic model to produce synthetic values of the transformed Gaussian variable. Monthly water quality events are then obtained by probability mapping from the Gaussian domain to the domain of the parent distribution. Detail simulation techniques are presented by McLeod and Hipel, 1978.

CONCLUSIONS

In an effort to obtain a greater understanding of the behaviour of toxic contaminants in the Thames river, research into the probability and stochastic features of phosphorous and suspended sediment concentrations have been performed. Mathematical models describing these features have been developed for monthly water quality events. Investigation in the probability behaviour of these events reveal that the governing probability distribution was not fixed for all months, but would change on a monthly basis. These distributions were also observed to be strongly non-Gaussian. The probability density functions were described using a five parameter polynomial expressions. This model successfully preserved the key moments (mean, variance, skewness, and kurtosis) of the historic water quality data.

Stochastic models for the phosphorous and suspended sediment concentrations were developed using the ARIMA process. Since this family of processes require that the underlying distributions for monthly events be Gaussian and time-invariant, novel

transformations methods were developed for mapping monthly water quality data from its parent distribution to a $N(0,1)$ distribution, for all months. The model constructed for the transformed monthly phosphorous variable was an ARIMA[1,1,0], with an autoregressive parameter estimate ϕ_1 of -0.546. Transformed suspended sediment data was adequately described using a white noise ARIMA[0,0,0] model.

The modeling methodology developed in this research serves to lay a solid framework for modeling water quality data from various streams. These data are likely to be non-Gaussian and represented by distributions that change monthly. The novel transformation developed in this research for such problems guarantees that the probability distribution of the actual series is incorporated in the model. Hence synthetic water quality events generated using these models are bound to reproduce the complex non-Gaussian time-varying probability distributions, while representing the serial relationship between consecutive monthly events. The foundation laid in this research also allows for stochastic models to be developed for data with substantial missing values, without having to make any assumptions about the character of the missing values. These developed models have the advantage of forecasting probable events for these missing zones, should these be necessary in future study.

REFERENCES

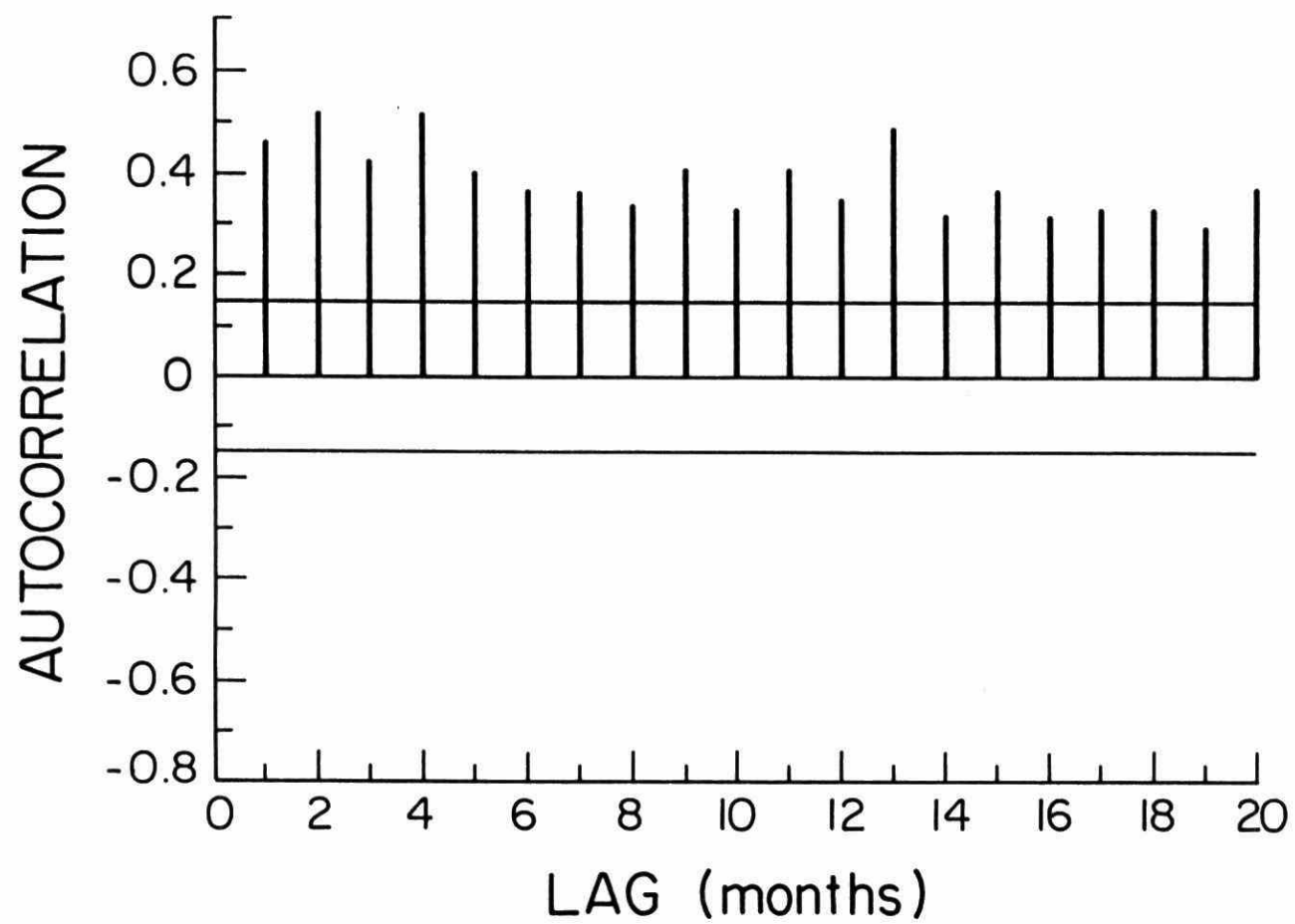
- Anderson, O.D. (1976). *Time series analysis and forecasting*. Butterworths, London and Boston.
- Atkinson, A.C. and M.C. Pierce (1976). The computer generation of beta, gamma, and normal random variables. *Journal Royal Statist. Soc. Ser. A*, 4, pp. 139 pp. 431-448.
- Bartlet, M.S. (1946). On the theoretical specifications of sampling properties of autocorrelated time series. *J. Royal. Statist. Soc. B*, 8, pp. 27-41.
- Blake, I.F. (1979). *An Introduction to Applied Probability*. Wiley. New Your, Toronto.
- Box, G.E.P., and G.M. Jenkins (1970). *Time Series Analysis: Forecasting and Control*. Holden-Day, San Fransisco.
- Box, G.E.P. and R.D. Cox (1964). An analysis of transformations. *Journal Royal Statist. Soc., B*, 26, pp. 211-252.
- Durbin, J. (1960). The fitting of time series models. *Rev. Int. Sttist. Inst.* 28, pp. 233-244.
- Frazer, D.A.S. (1976). *Probability and Statistics: Theory and Application*. Wadsworth Publishing Co., Inc. Belmont, California, 94002.
- Hipel, K.W. and A.I. McLeod (1979). Modeling seasonal geophysical time series. Technical report no. Xm030579, University of Waterloo.
- Hipel, K.W., A.I. McLeod, and W.C. Lennox (1977). Advances in Box-Jenkins modelling, 1, model construction. *Water Resource Research* 13, pp. 567-575.
- Lewis, P.A.W., A.S. Goodman, and J.M. Miller (1969). Pseudo-random number generator for the System 360. *IBM System Journal*. 8, pp. 136-146.
- Marsaglia, G. and T.A. Bray (1964). A convenient method for generating normal variables. *SIAM Rev.* 6, pp. 260-264.
- McLeod, A.I. and K.W. Hipel (1978). Simualtion procedure for Box-Jenkins models. *Water Resources Research*. 14, pp. 969-975.
- Pagano, M. (1973). An algorithm for fitting autoregressive schemes. *Journal Royal Statist. Soc. Ser. C*. 21, pp. 274-281.
- Quenouille, H.M. (1949). Approximate tests for correlation in time series. *Journal Royal Stat. Soc., B11*, pp. 68.
- Snedecor, G.W. and W.G. Cochran (1980) *Statistical Methods*. IOWA State University Press.
- Strecok, A.J. (1968). On the calculation of the inverse error function. *Mathematics of Computing*, 22, pp. 144-158.

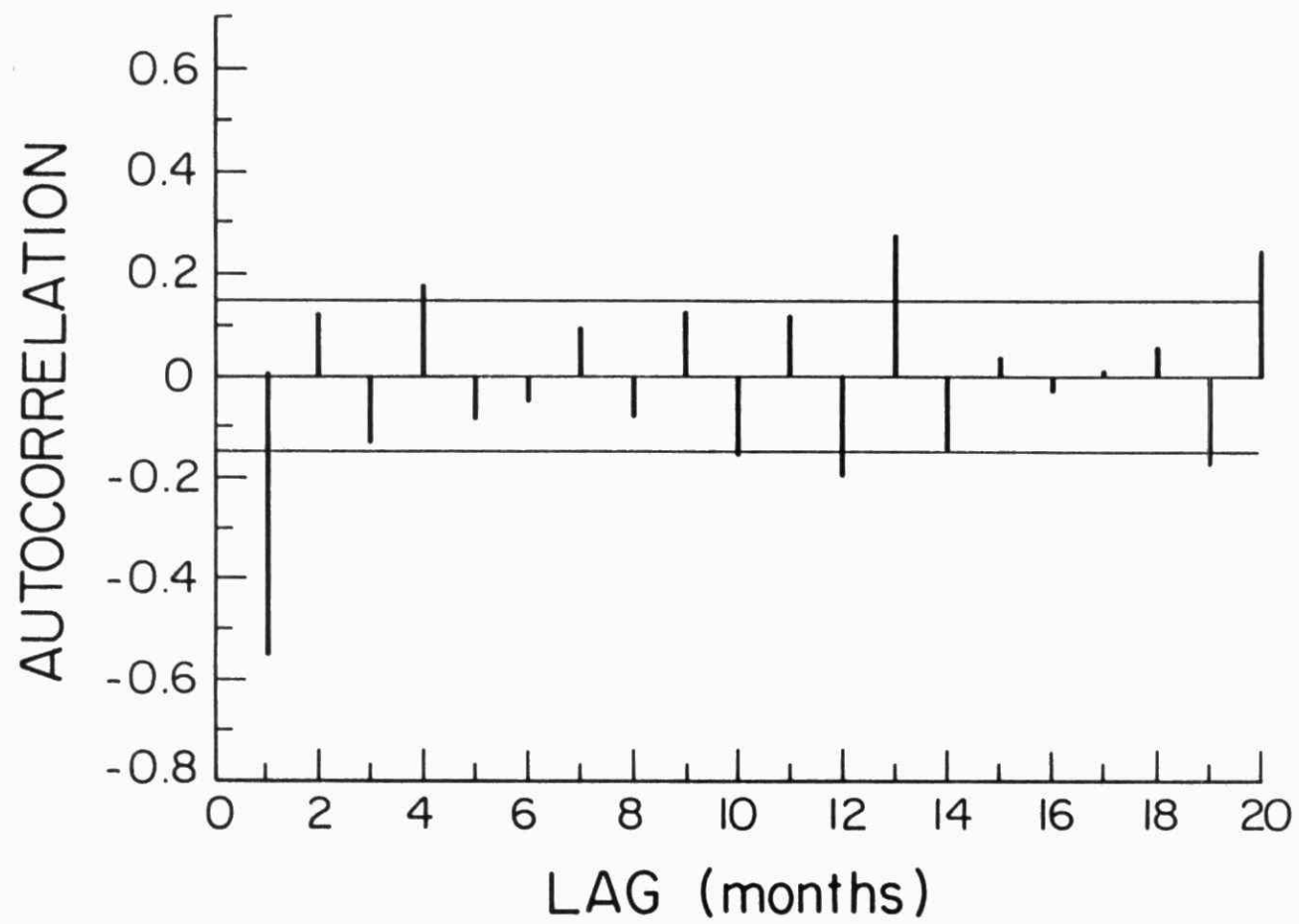
Tao, P.C. and J.W. Delleur (1975). Models of the stochastic and chronologic structure, prediction and simulation of run off sequences-applied to the lower OHIO basin. Purdue University, Water Resources Center. West Lafayette, Indiana. Report #60.

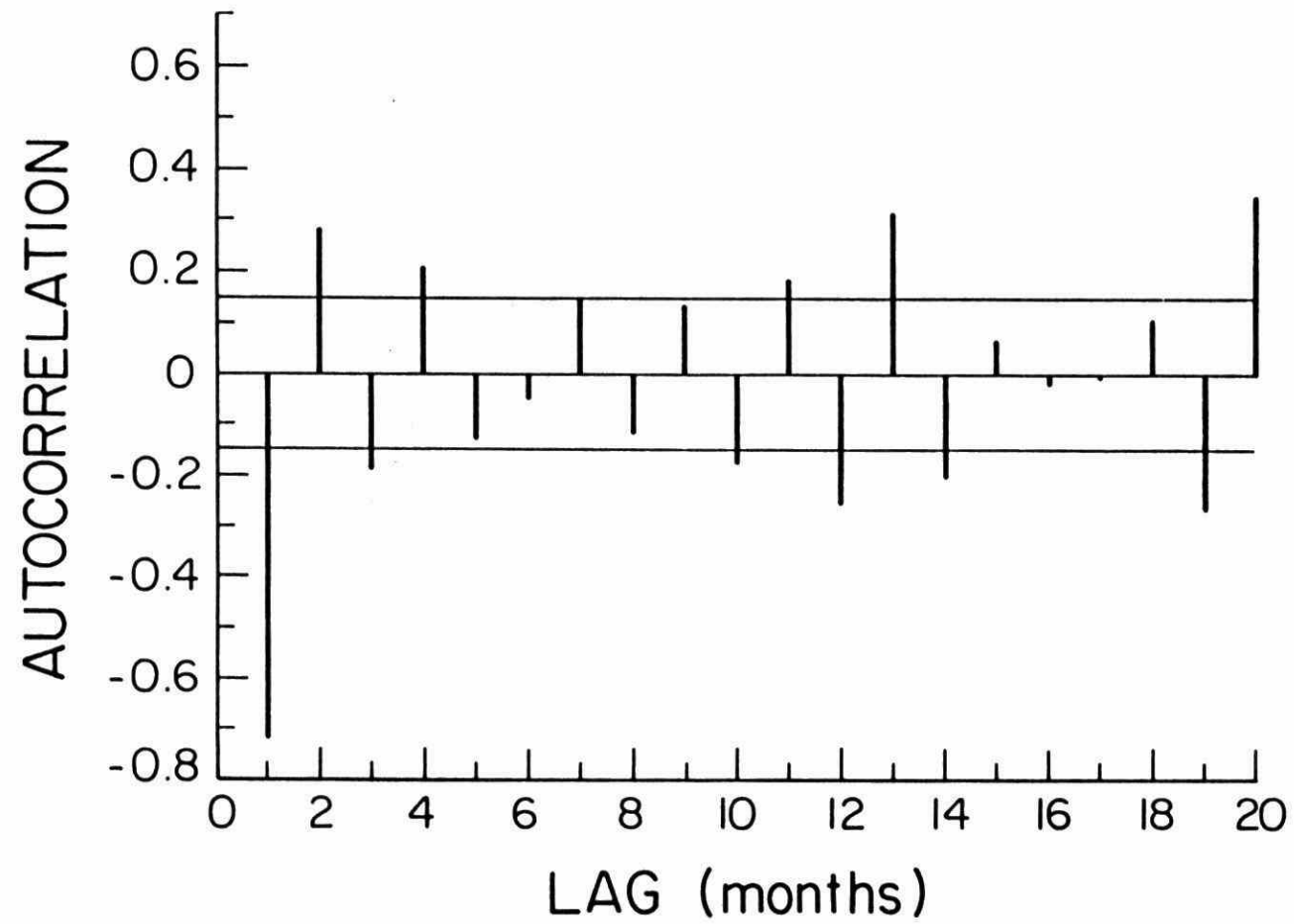
Unny, T.E. (1977). Stochastic precesses in water resources engineering. Proc. 2nd. Int. IAHR Symposium on Stochastic Hydraulics, Lund Inst. of Technology. University of Lund. Lund, Sweden.

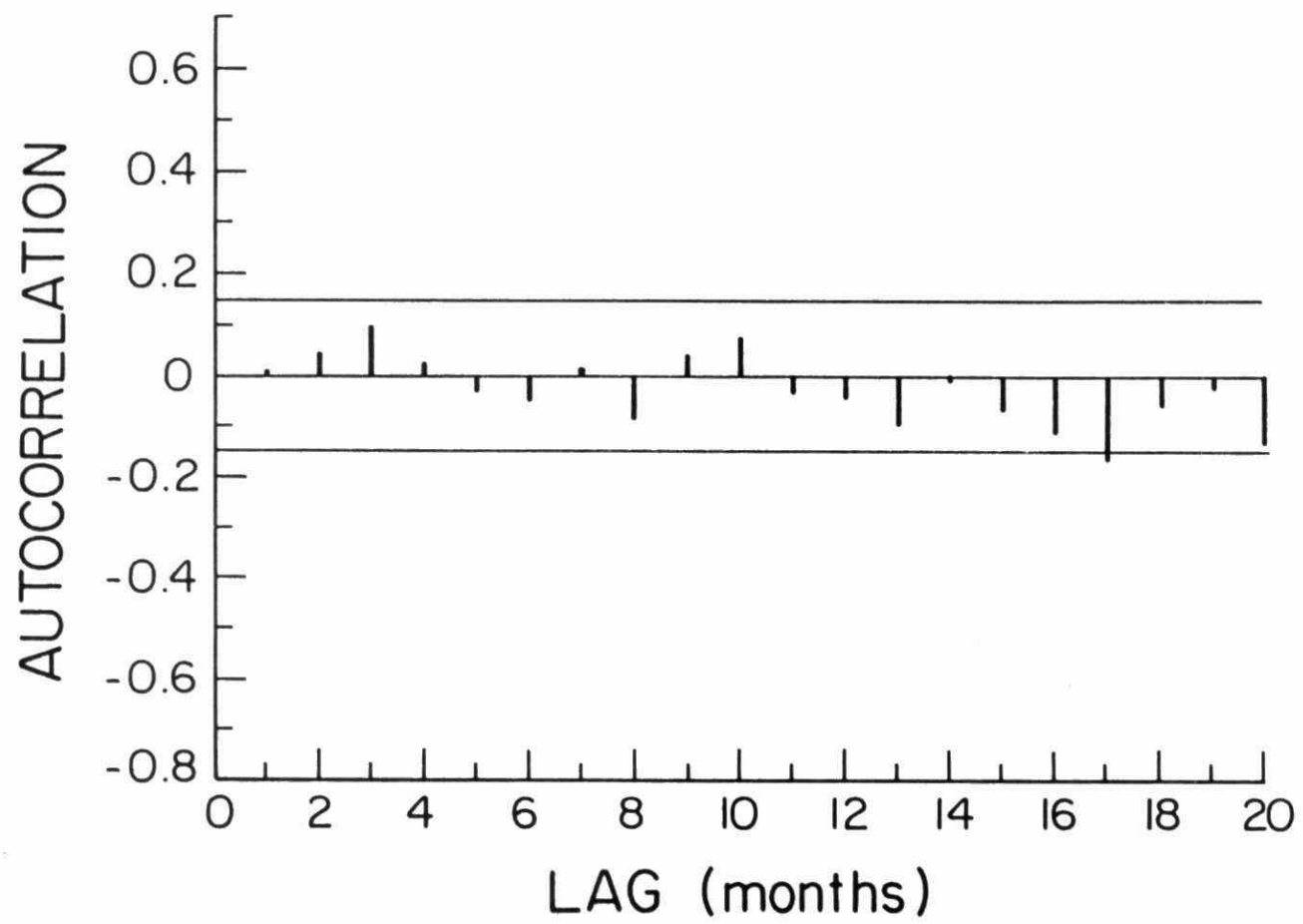
LIST OF FIGURES

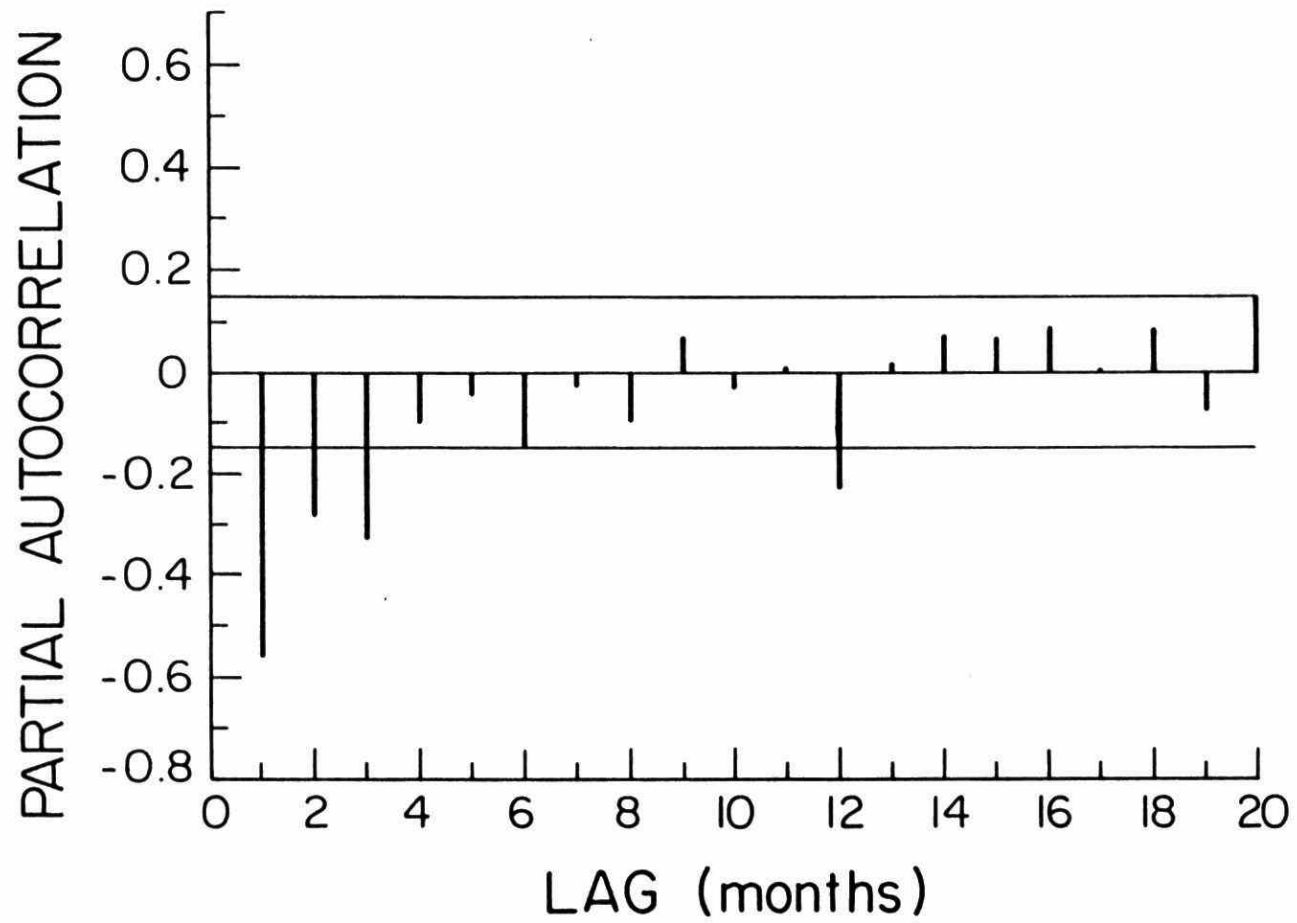
1. Plot of Autocorrelation Function vs Month (Lags)
for Transformed Monthly Phosphorous Data
2. Plot of Autocorrelation Function vs Month (Lags)
for Once Differenced Transformed Monthly Phosphorous Data
3. Plot of Autocorrelation Function vs Month (Lags)
for Twice Differenced Transformed Monthly Phosphorous Data
4. Plot of Autocorrelation Function vs Month (Lags)
for Transformed Monthly Sediment Data (Thames River)
5. Plot of Partial Autocorrelation Function vs Month (Lags)
for Once Differenced Transformed Monthly Phosphorous Data
6. Plot of Partial Autocorrelation Function vs Month (Lags)
for Transformed Monthly Sediment Data

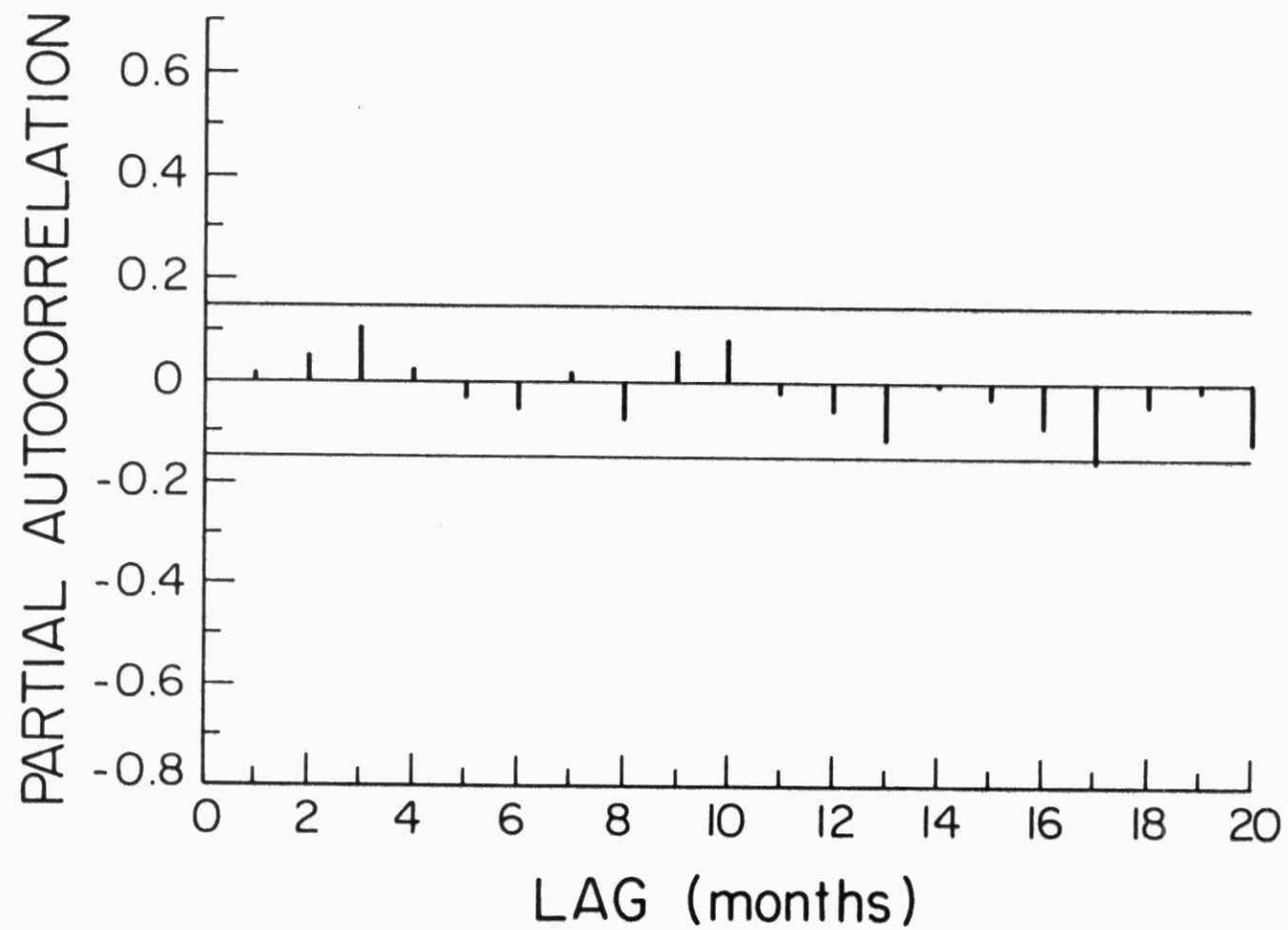












OTTAWA RIVER NUCLEAR SPILL CONTINGENCY MODEL DEVELOPMENT - PHASE II

by

Rob Jarvis
Gore & Storrie

ABSTRACT

The purpose of the Ottawa River spill model development is to allow contingency planning in the case of a nuclear (probably tritium) spill from the Rolphton nuclear power demonstration (NPD) facility. A model which simulates the two-dimensional - downstream and cross-stream - flow of pollutant already exists in the form of the FORTRAN 77 program TWODIFIN. The purpose of the Phase II Study is to extend this program.

As part of the Phase II Study, a one-dimensional version of the spill model has been developed and implemented in the computer program ONEDIFIN. This is a one-dimensional model - that is, it treats the river as a one-dimensional line and thus assumes complete lateral mixing of pollutant - that can be used to speed up calculations when the pollutant is laterally well-mixed. It is a multiple-source model, so that it can handle simultaneous spills from different locations, and it allows for first-order decay of the radioactive material.

Another major part of the Phase II Study was to interface the one- and two-dimensional programs. In such a hybrid program, the two-dimensional model would be used only for the portion of river that is not laterally well-mixed. Elsewhere, the one-dimensional model would be used, increasing the speed and efficiency of the calculations. This program has been developed and exists in single- and multiple-source versions - ONETWO and OTMULT, respectively.

Along with the main modelling portions, the study also involved the development of computer graphics and other programs to make the model interactive and easy to use. This is proceeding and it is hoped that the graphics will play a major role in helping to analyze and deal with potential spills. Also, model calibration is being performed using field data from the 1981 tritium spill from the Rolphton NPD.

INTRODUCTION

As part of the Ottawa River nuclear spill contingency planning studies, a model which will aid in predicting the arrival times, duration of passage, and concentration distributions of the spilled radionuclide at the water supply intakes and other strategic locations has been developed. This mathematical model consists of a finite-time analytic model that predicts concentration distributions in 2 spatial dimensions (2-D), namely downstream (longitudinal) and cross-stream (lateral). Output from this model can be viewed in two formats i) as a 2-D distribution at a specified time (Figure 2) or ii) as a time varying cross stream distribution at a particular location downstream from the spill.

When the cross-stream distribution reaches a constant value (within a certain margin of deviation) that is, the radionuclide becomes laterally well mixed the computer program switches to a computationally faster algorithm; a one-dimensional (1-D) finite time model. The one-dimensional part of the computer program varies in time and downstream or longitudinal dimension. Both the 2-D and 1-D are vertically averaged models, that is, the spill material is considered to be vertically well mixed and vertical concentration gradients do not exist.

The remaining objectives of this study are to

- 1) make the program user-friendly
- 2) present the model outputs in graphical form
- 3) perform a calibration and a verification using tracer study data and data from the tritium spill at Rolphoton nuclear power demonstration (NDP) facility in 1981.

MODEL FORMULATION

One-Dimensional Spill Model

ONEDIFIN is a Fortran program that produces one-dimensional but time dependant concentration distributions in shallow rivers. This time dependancy allows the modelling of spill events, that is time varying discharges of contaminant into a river. The solution gives concentrations dependent only on the distance downstream from the source of the spill and hence assumes the pollutant to be laterally well-mixed.

The governing equation for the one-dimensional model is:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = e_x \frac{\partial^2 c}{\partial x^2} - K_d c \quad (1)$$

where x = longitudinal co-ordinate (m)

t = time (s)

u = velocity downstream (m/s)

e_x = longitudinal dispersion coefficient (m²/s)

K_d = first order decay rate coefficient (1/s)

c = concentration at location (x) and time (t)

This equation assumes complete vertical and transverse mixing in the river consequently the model, as a whole, is restricted in its application. Generally, the longitudinal distances required to achieve complete vertical and lateral mixing are in the range 50 to 100 times depth and 50 to 100 times width of channel, respectively; for the Ottawa River segment below the Rolphton NDP discharge, the corresponding distances are estimated to be 0.345 and 42.66 km (Gore & Storrie Ltd. 1983). If there is any uncertainty, a two-dimensional model can be used to determine when the river becomes laterally mixed (vertical mixing will already have occurred by this point downstream).

The solution to the equation under a release of pollutant of constant discharge and concentration is:

ONEDIFIN TEST RUN FOR OTTAWA RIVER

TRITIUM SPILL FROM ROLPHTON, AUG 17-25, 1981

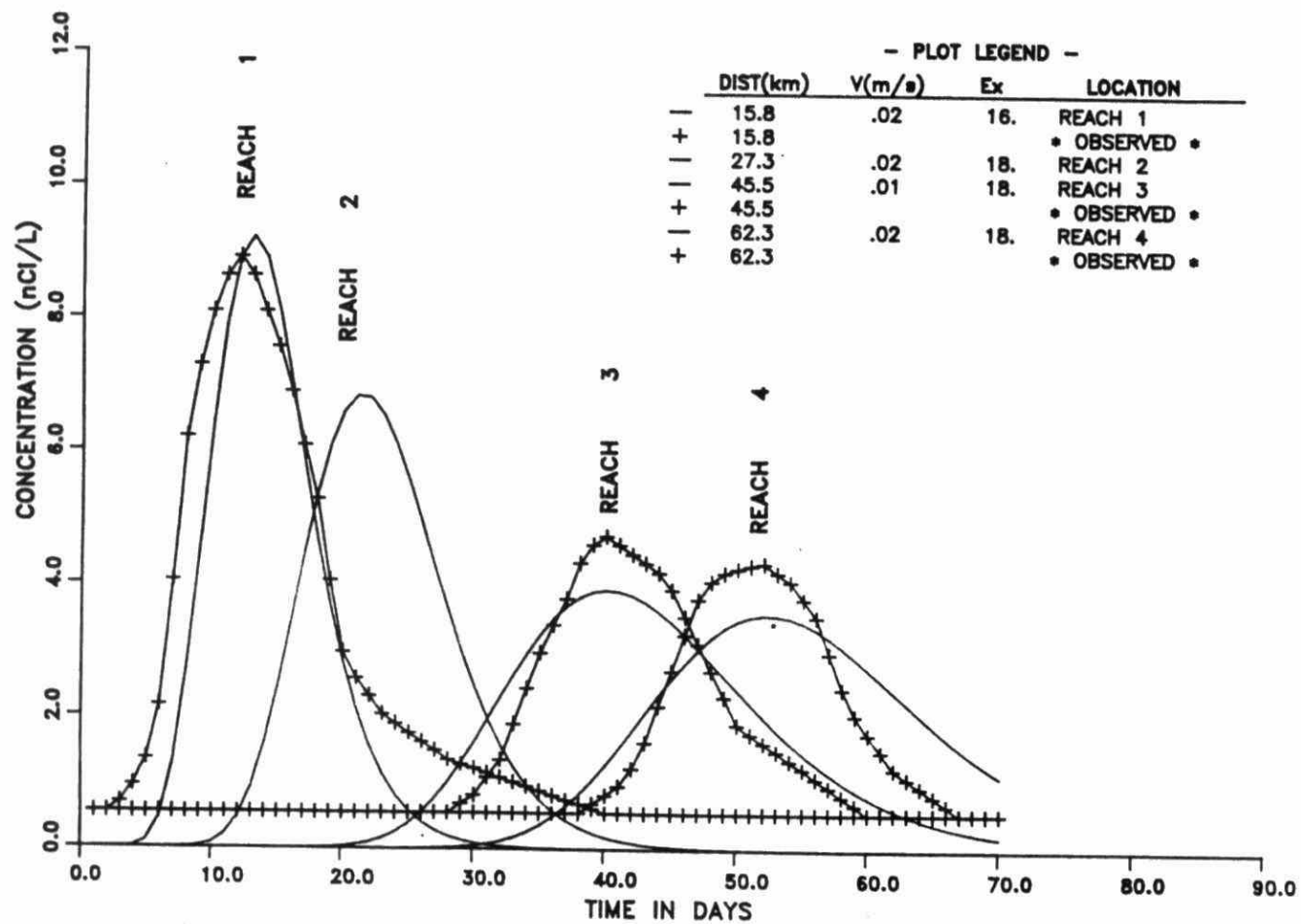


FIGURE 1
Output from model
ONEDIFIN

$$c = \frac{w}{2Au} e^{(ux/e_x)} \left\{ \begin{aligned} & - 471 - \\ & \operatorname{erf} \left(\sqrt{\frac{a}{t-t_i}} + \sqrt{b(t-t_i)} \right) \\ & - \operatorname{erf} \left(\sqrt{\frac{a}{t-t_j}} + \sqrt{b(t-t_j)} \right) + \operatorname{erf} \left(\sqrt{\frac{a}{t-t_j}} - \sqrt{b(t-t_j)} \right) \\ & - \operatorname{erf} \left(\sqrt{\frac{a}{t-t_i}} - \sqrt{b(t-t_i)} \right) \end{aligned} \right\} \quad (2)$$

$$\text{where } a = x^2/4e_x \quad (2a)$$

$$b = (u^2/4e_x) + K_d \quad (2b)$$

$$w = c_0 q_0 \quad (2c)$$

and x = distance from source (m)

t = time (s)

c_0 = concentration of source release

q_0 = discharge of source (m^3/s)

A = cross-sectional area of flow (m^2)

u = velocity of flow (m/s)

e_x = longitudinal dispersion coefficient

t_i = time of the start of the release (s)

t_j = time of the end of the release (s)

To obtain a complete solution, it is necessary to break the release of pollutant up into short intervals such that the discharge and concentration is relatively constant over each. Using the linearity of Equation 1, these partial solutions can be summed for each (x,t) (See Figure 1).

In ONEDIFIN, each reach is treated in isolation, with a "source" at the beginning and the concentration calculations being made at the end. The mass discharge value, w , from Equation 2 is determined for each reach by combining the calculated results from the previous reach and the inputs from any new sources at the beginning of the reach. In other words, the flow of pollutant from the previous reach is treated as a source and added to the flow from any other sources. This technique is much faster than superposition when multiple sources are being considered.

Two-Dimensional Spill Model

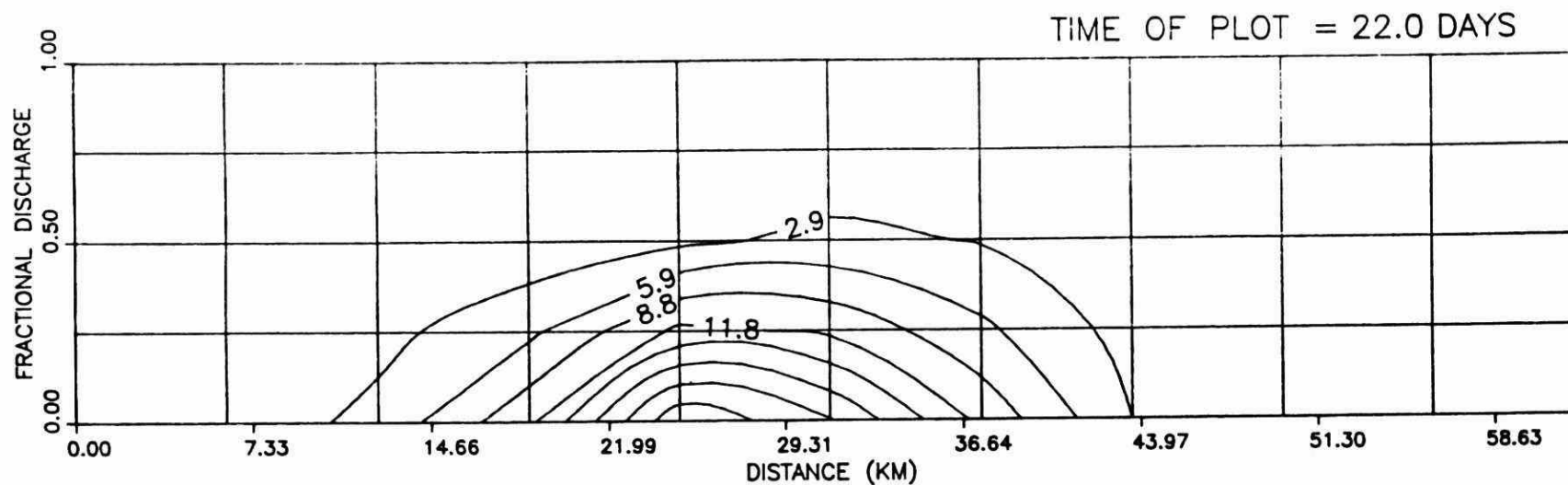
TWODIFIN is an acronym for TWO-Dimensional FINite-time model. The "two-dimensional" part refers to the two spatial dimensions that it considers - the longitudinal or downstream dimension and the lateral or cross-stream dimension. As in the case of ONEDIFIN, the finite-time part refers to the fact that the model is driven by a spill event (see Figure 2).

This model is made tractable through the use of a transformation in the lateral dimension known as the stream tube method. The fundamental concept of the stream tube model developed by Yotsukura and Cobb (1972) is that it uses the cumulative partial discharge, q , at a given cross-section instead of the lateral discharge, y , as independent variable. In this approach, the cross-section is divided into a number of vertical strips termed "stream tubes" such that the discharge within each stream tube is equal. Thus, the cross-sectional concentration distributions $c(x,q)$, predicted by the stream tube model will be functions of q . These distributions can be transformed into $c(x,y)$ as a function of distance from the bank, y , by knowing the relation between q and y at each transect.

The derivations of the basic equations of the stream tube model have been presented by Yotsuhura and Cobb (Ibid); they are subject to the following assumptions.

1. The density of the effluent (or solute) is the same as that of the receiving water. This assumption is reasonably satisfactory for most of the municipal effluent discharges to rivers.
2. The concentration distributions in the far field are not effected by the near field mixing processes (eg. dilution due to initial momentum of jet). Usually, the jet-induced diffusion approaches the ambient diffusion for a short distance below a source in a shallow river.
3. The depth distribution of effluent in the river channel is uniform. Generally the longitudinal distance required to attain depth uniformity is short in shallow rivers, being of the order of 50 to 100 times the channel depth; thus, this assumption is justified.

SPILL MODEL 'TWODIFIN' - OTTAWA RIVER



- 473 -

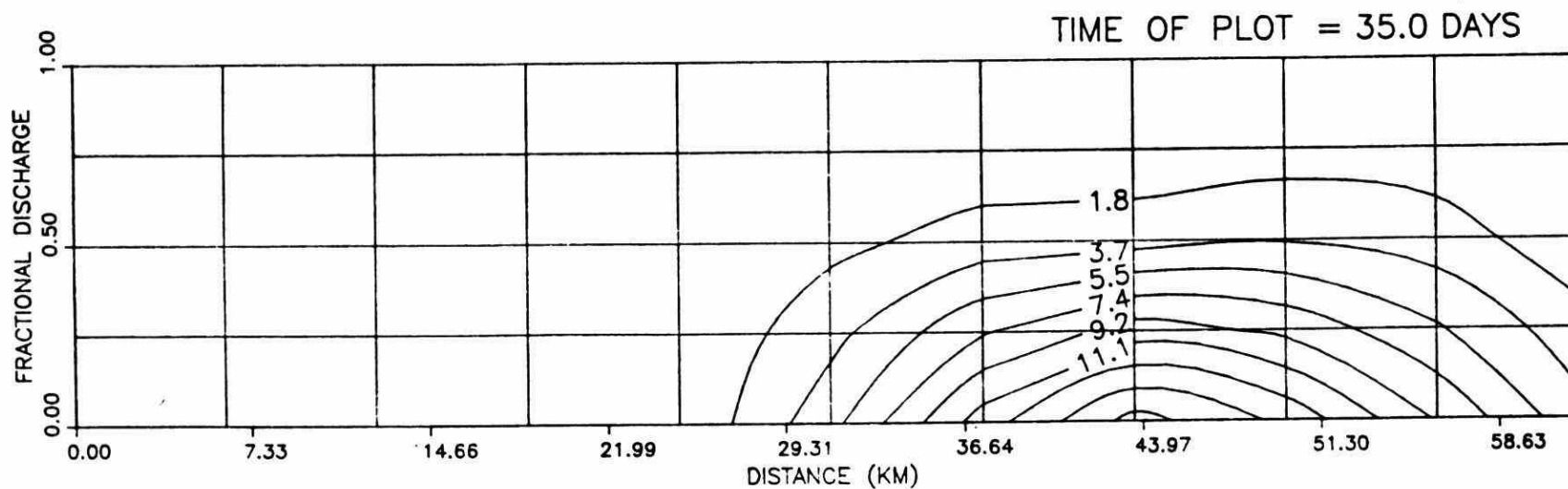


FIGURE 2 Output from model TWODIFIN

The Convective - Dispersion Equation

The 2-D convective-dispersion equation for a non-conservative material in the far field region of the mixing zone can be written in the form:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = e_x \frac{\partial^2 c}{\partial x^2} + u D_y \frac{\partial^2 c}{\partial q^2} - K_d c \quad (1)$$

where x = longitudinal co-ordinate (m)
 q = lateral co-ordinate (m^3/s)
 t = time (s)
 u = velocity of flow in the x direction (m/s)
 e_x = longitudinal dispersion coefficient (m^2/s)
 D_y = lateral diffusion factor (m^5/s^2)
 K_d = first order decay rate coefficient (1/s)
 c = concentration at point (x,q) at time (t)

The solution to the equation under a release of pollutant of constant discharge and concentration is:

$$C = \frac{u}{4} \cdot \frac{\exp(\frac{ux}{2e_x}) \cdot W}{\sqrt{\pi e_x e_q}} \cdot \frac{\exp(-2\sqrt{ab})}{(ab)^{1/4}} \left\{ \operatorname{erf}\left(\sqrt{\frac{a}{t-t_j}} - \sqrt{b(t-t_j)}\right) - \operatorname{erf}\left(\sqrt{\frac{a}{t-t_i}} - \sqrt{b(t-t_i)}\right) \right\} \quad (2)$$

$$\text{where } a = (x^2/4e_x) + ((q_s - q)^2/4e_q) \quad (2a)$$

$$b = (u^2/4e_x) + K_d \quad (2b)$$

and u = velocity of flow (m/s)
 x = distance downstream from source (m)
 t = time (s)
 t_i = time of beginning of release (s)
 t_j = time of end of release (s)
 w = rate of release of mass (1/s)
 e_x = longitudinal dispersional coefficient (m^2/s)
 e_q = transverse diffusion coefficient (m^6/s^3)

The transverse diffusion coefficient is calculated in the TWODIFIN model using the relation:

$$e_q = \beta Q^2 u / b \quad (3)$$

where Q is the total discharge for a reach and β is a dimensionless factor to be estimated from field river data. This can be done by making several runs of the model with different β -values and choosing the value that produces the most realistic lateral mixing distance. Typically, its value ranges from .0005 to .01 (see Appendix A).

As in the case of the 1-D model, a complete solution for a spill with time-varying discharge and concentration can be developed by breaking the spill into small elements and summing the result of Equation 2 for each element.

The program TWODIFIN considers sidewall reflection effects using the method of images.

In TWODIFIN, the river is divided longitudinally into reaches, and laterally into stream tubes. Each reach should be a river section of fairly constant hydrodynamic characteristics; TWODIFIN uses constant dispersion coefficients within each reach. The position of the stream tube boundaries are determined only at transects where the velocity, depth and width measurements have been surveyed.

TWODIFIN considers only a single source, at the beginning of the first reach. The reaches are not treated independently, as they are in ONEDIFIN, where the pollutant flow from the previous reach serves as the "source" for the current one. Instead, the concentration is calculated for each reach from the flow of pollutant from the source all the way to the end of the reach. To take into account the variation of hydrodynamic parameters from reach-to-reach, moving averages are maintained that approximate the effective values of river width, depth, and velocity of flow.

Hybrid Spill Model

Aside from ONEDIFIN and TWODIFIN, there is also a hybrid spill model, ONETWO. In this program, calculations are made according to the 2-D model until the river becomes well-mixed, at which point the 1-D model is used. This is useful for studying long rivers, in which lateral mixing occurs a short distance downstream in relation to the total length studied, because the 1-D model is much faster than the 2-D version.

Like the two other models mentioned above, ONETWO is a finite-time model. It is also a multiple source model which, unlike ONEDIFIN, accepts sources placed anywhere along the river. The resulting concentration predictions are obtained by superposition method (explained below). This method has disadvantages: principally, it is slower than the method used in ONEDIFIN, by a factor equal to the number of sources used. However, it separates source placement from reach definition, which are unrelated procedures, and it does not suffer the mass-loss problems encountered by ONEDIFIN when going from reach to reach.

ONETWO calculates the pollutant distribution using the method of superposition. That is, it considers each source separately and determines the concentration distribution which that source would cause if it were the only one on the river. It then sums these distributions (by algebraically summing the concentration predictions together for each location and time) to obtain the complete solution. This can be done whether a 1-D or 2-D model is being used. This approach is justified because the equations are linear in concentration.

The criterion that ONETWO uses to determine the reach at which the river becomes well-mixed involves a simple ratio test. Specifically, when the ratio between the minimum and maximum concentrations across the river for that reach is greater than some tolerance value, the river is said to be well mixed. This tolerance will usually have a value of 0.8 or 0.9.

APPENDIX A

EVALUATION OF DISPERSION COEFFICIENTS

Two dispersion coefficients are used in the spill model. The longitudinal coefficient determines the downstream spread of the pollutant and the lateral dispersion coefficient determines the cross-stream spread. The lateral coefficient is used only in the two-dimensional model.

The longitudinal dispersion coefficient e_x has units m^2/s . There are several different methods for calculating e_x but in the context of this model it becomes primarily a matter of empirical calibration. The user adjusts e_x in the model reach by reach until predictions match observed data. The model is set-up so that after an e_{x1} has been determined at a measured total river flow Q_1 , e_{x2} can be determined knowing a different total flow Q_2 . This scale up method was derived from the Leopold-Maddock relationships. According to

$$e_x = 22.6 n \bar{u} \bar{d}^{5/6} \quad (A.1)$$

where n = Manning's "n" $(m^{1/6})$
 \bar{u} = average water velocity
 \bar{d} = average depth

The Leopold-Maddock relationships are;

$$\bar{u} = bQ^{vex} \quad \text{or} \quad \bar{u}_2 = \bar{u}_1 (Q_2/Q_1)^{vex} \quad (A.2)$$

$$\bar{d} = cQ^{hex} \quad \text{or} \quad \bar{d}_2 = \bar{d}_1 (Q_2/Q_1)^{hex} \quad (A.3)$$

$$W = eQ^{wex} \quad \text{or} \quad W_2 = W_1 (Q_2/Q_1)^{wex} \quad (A.4)$$

where $\bar{u}\bar{d}w = Q$ and w is top width.

The parameters VEX, HEX and WEX are determined empirically and must sum to unity. From equations A.1, A.2 and A.3 we get

$$e_{x2} = e_{x1} \left(\frac{Q_2}{Q_1} \right)^{vex + 5/6 hex}$$

Typical values for a shallow river are

$$\text{HEX} = .50$$

$$\text{VEX} = .45$$

$$\text{WEX} = .05$$

and therefore

$$ex_2 = ex_1 (Q_2/Q_1)^{.8667}$$

The lateral dispersion coefficient has units m^6/s^3 . TWODIFIN calculates it using the equation

$$e_q = \beta Q^2 u / b \quad (2)$$

where e_q = lateral dispersion coefficient (m^6/s^3)

β = dimensionless dispersion factor

Q = discharge of the river (m^3/s)

u = velocity of flow (m/s)

b = river width (m)

Like the regional dispersion factor in Equation 1, the factor, β , is essentially a calibration factor, which in this case, adjusts the lateral dispersion coefficient to a more realistic value. It can be determined by any of a number of relationships, but these are not always reliable. If some actual river data is available, it will probably be more accurate to use trial-and-error.

Trial-and-error estimation of e_x can be done in a couple of ways. If actual dispersion coefficients are known for the river in question, it is a simple matter to solve for the appropriate β -values (β is not a constant - it can vary with respect to downstream distance). If concentration profiles are known from direct measurement, the TWODIFIN model can be run with different β 's, and those that give the best prediction can be selected.

REFERENCES

- Bansal, M.K., 1971. Dispersion in Natural Streams. Journal of Hydraulics Division, ASCE, 97 (HY11): 1867-1886.
- Beltaos, S., 1979. Transverse Mixing in natural Streams. Canadian Journal of Civil Engineering. 6 (4): 575-591.
- Fisher, H.B., 1967. The Mechanics of Dispersion in Natural Streams. Journal of Hydraulics Division, ASCE, 93 (HY6): 187-216.
- Glover, R.E., 1964. Dispersion of Dissolved or Suspended materials in Flowing Streams. U.S. Geol. Survey Prof. Paper 433-B, 32 p.
- Gore & Storrie, Ltd., 1983. Dispersion Estimates for the Ottawa River Nuclear Spill Contingency Model. Technical Report prepared for the Ontario Ministry of the Environment, Toronto, Ontario. 34 p.
- Gowda, T.P.H., 1980. Stream Tube Model for Water Quality Prediction in Mixing Zones of Shallow Rivers. Water Resources Paper 14, Water Resources Branch, Ontario Ministry of the Environment, Toronto.
- Gowda, T.P.H., 1981. Water Quality Prediction in Shore-Attached Mixing Zones in Rivers. An Assessment Procedure prepared for Working Group II of the Water Management Steering Committee, Ontario Ministry of the Environment, Toronto, Canada, 59 p.
- Gowda, T.P.H., 1984a. Critical Point Method for Mixing Zones in Rivers. Journal of Environmental Engineering, ASCE, 110 (1): 244-262.
- Gowda, T.P.H., 1984b. Water Quality Prediction in Mixing Zones of Rivers. Journal of Environmental Engineering, ASCE, 110 (4): 751-769.
- Hamdy, Y., 1981. Dispersion of Effluent Plumes from Diffusers on Near-Shore Regions of the Great Lakes, Vol. 1 - Initial Mixing Processes. Ontario Ministry of the Environment, Toronto.
- Heathcote, I.W., 1982. Spills Dispersion. Grand River Basin Water Management Study, Technical Report No. 31, Water Resources Branch, Ontario Ministry of the Environment, Toronto (Draft).
- Henry, J.F., and Foree, E.G., 1979. Dispersion Modelling in Time and Two Dimensions. Journal of the Environmental Engineering Division, ASCE, 105 (EE6): 1131-1147.
- McQuivey, R.S. and Keefer, T.N., 1976. Convective Model of Longitudinal Dispersion. Journal of Hydraulics Division, ASCE, 102 (HY10): 1409-1424.
- Medina, M.A., Jr. and Buzun, J., 1981. Continuous Simulation of Receiving Water Quality Transients. Water Resources Bulletin, 17 (4): 549-557.

- Sagar, B., 1982. Dispersion in Three Dimensions: Approximate Analytic Solutions. Journal of Hydraulics Division, ASCE, 108 (HY1): 47-62.
- Wnek, W.J. and Fochtman, E.G., 1972. Mathematical Model for Fate of Pollutants in Near-Shore Waters. Environmental Science and Technology, 6 (4): 331-337.
- Yotsukura, N. and Cobb, E., 1972. Transverse Diffusion of Solutes in Natural Streams. U.S. Geological Survey Professional Paper 582-C, U.S. Government Printing Office, Washington, D.C., 19 p.
- Yotsukura, N. and Sayre, W., 1976. Transverse Mixing in Natural Channels. Water Resources Research, 12 (4): 695-704.

TD
172.5
.057
1986
part B

Proceedings : technology
transfer conference
76021

TECHNOLOGY TRANSFER CONFERENCE 1986

Organized by RESEARCH ADVISORY COMMITTEE
J. Pagel, Chair

Sponsored by CORPORATE RESOURCES DIVISION
A. Castel, Executive Director

CONFERENCE COMMITTEE:

Environment Ontario:	M. Moselhy	Co-ordinator
	D. Bartkiw	G. Rees
	W. Chan	R. Reguly
	J. Donnan	G. Ronan
	D. McTavish	C. Schenk
	E. Piché	
Labour Ontario:	G. Wright	
Health Ontario:	L. Smith	
Environment Alberta:	H. Sims	
Environment Québec:	H. Saint-Martin	
Environment Canada:	F. Hurtubise	K. Shikaze
	B. Jank	
University of Waterloo:	J. Cherry	
Lakehead University:	G. Ozburn	
Goodfellow Consult. Inc.:	H. Goodfellow	
Zenon Environmental Inc.:	A. Benedek	
Communications:	T. Gorsline	C. Labonté
Poster Session:	H. Eijssenck	
Spouse Program:	Ann-Marie Clarke	